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CONTRIBUTIONS
FROM
THE PHYSICAL LABORATORY
OF
THE UNIVERSITY OF MICHIGAN

Number 1.



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(Reprinted from *Physical Review*, Sept. 1911)
2. A. G. Worthing: Some Thermodynamic Properties of Air
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Ann Arbor, Mich.

April, 1913.

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HEAT OF EVAPORATION OF WATER.

BY ARTHUR WHITMORE SMITH.

THE "heat of evaporation" of water means the heat per gram required to change water into saturated vapor at the same temperature. Various determinations of this value have been made during the past century,¹ the most extensive investigation being the work of Regnault² over sixty years ago. In the older methods steam from a boiler was passed directly into a calorimeter, where it was condensed. The heat of condensation was measured by the increase in temperature of the cold water of the calorimeter, while the amount of vapor was determined by weighing the condensed water. In more recent experiments the water was boiled in the calorimeter, a known amount of heat being supplied by an electric current. The amount of water thus removed from the calorimeter was determined either by the loss in weight of the containing vessel,³ or by condensing the steam and weighing the water thus collected.⁴

It is now well known among mechanical engineers that the vapor rising from boiling water carries with it a certain amount of water in a finely divided state, but nevertheless still liquid. The amount of water thus carried in the steam is often over one per cent., and it may be several per cent. of the whole. This leads one to inquire what quality of steam was used in previous experiments to determine the heat of evaporation. If the steam used contained 1 per cent. of moisture it is evident that the familiar number 537 is 1 per cent. too low.

Regnault appears to have known something of the difficulty of obtaining dry steam, and in his classical experiments collected the steam by means of a long tube coiled in the upper part of his boiler. It is now known that this precaution is not sufficient. The later determinations by Joly⁵ with a "steam calorimeter," and by Henning vigorously boiling water in a small calorimeter⁶ with no separator, certainly were made with steam containing an uncertain amount of moisture.

¹ See Preston, *Theory of Heat*, p. 378 ff.

² Regnault, *Institute de France, Mem. Acad. Sci.*, Vol. 21, pp. 1-748, 1847.

³ Griffiths, *Phil. Trans.*, Vol. 186 A, pp. 261-342, 1895.

⁴ A. W. Smith, *Phys. Rev.*, Vol. 25, pp. 147-170, 1907. Henning, *Ann. der Phys.*, Vol. 21, pp. 849-878, 1906; Vol. 29, pp. 441-465, 1909.

⁵ Joly, *Phil. Trans.*, Vol. 186 A, note on p. 322, 1895.

⁶ Henning, *loc. cit.*, Fig. 1, p. 446.

It is the object of this research to determine the heat of evaporation of water at the boiling point more exactly than has yet been done, and especially to eliminate this serious error which apparently has gone unnoticed. The practical need of knowing the exact value of this constant is evident, since it is the basis of the steam tables used in all problems in steam engineering, and a change in this value means a corresponding change throughout the steam tables.

The relative values of the heat of evaporation at different temperatures have been well established by the recent investigation by Davis¹ on the results obtained in experiments on the free expansion of dry steam. Unfortunately the absolute value at any point on his curve is unknown, and steam tables² based on this curve assume for the value at 100° C. the mean of the results obtained by Joly and by Henning.

If a reliable determination of the heat of evaporation can be obtained at any one temperature it will have the effect, through this curve, of establishing its value throughout the range of temperatures used in steam engineering.

As far as I am aware, no attempt has ever been made to determine the heat of evaporation from a quiet surface of water. Evaporation from such a smooth surface is supposed to take place by one molecule at a time leaving the liquid and going into the vapor. The action inside of a steam boiler is very different from this, and it would be surprising not to find some fine spray thrown into the steam. It is from this point of view that the problem has now been attacked.

METHOD.

A gentle stream of dry air is drawn through the calorimeter, passing over the unruffled surface of the hot water and carrying away some of the vapor. Near the boiling point water evaporates very readily, and care must be exercised not to overcool the calorimeter by too rapid evaporation. Heat is supplied by an electric current, and the air current is constantly regulated to allow the evaporation to proceed just fast enough to keep the temperature constant at 98° C. After passing out of the calorimeter most of the vapor is condensed in a cold flask, while the remainder is caught by drawing the air through sulphuric acid. The gain in weight gives the amount of water evaporated in the calorimeter.

The heat received by the calorimeter is that generated in the heating coil plus a small amount which comes from the surroundings by radiation

¹ Davis, *Journ. Am. Soc. Mech. Eng.*, No. 1212, Vol. —, pp. 1419-1452.

² Marks and Davis, *Steam Tables*, Longmans, 1909.

and conduction. The latter cannot be measured directly, but it can be eliminated in the computations by the following method. Each result is computed from two experiments, in one of which a large amount, and in the other a much smaller amount of water is evaporated. The temperatures and other conditions are the same in each and so also is the amount of heat received from the outside. Therefore the difference between the two total amounts of heat eliminates these corrections and is the same as the difference between the two amounts of heat delivered by the current alone. This difference, divided by the difference between the corresponding amounts of water, gives the heat per gram necessary to evaporate water at this temperature.

Thus let M' denote the number of grams of steam produced in a given experiment, H' the corresponding amount of heat supplied by the current, and h the small amount of heat gained by radiation, conduction, etc. Then

$$H' + h = LM', \quad (1)$$

where L is the heat of evaporation. On another day the experiments are repeated under the same conditions as before, but using a larger amount of heat. Then

$$H'' + h = LM'', \quad (2)$$

and combining these two equations by subtraction gives

$$L = \frac{H'' - H'}{M'' - M'}. \quad (3)$$

All corrections for heat gained by radiation or conduction, whether known or unknown, are eliminated by this method of differences. There were no starting or stopping corrections, as each experiment, so called, was a one hour section from the middle of an all day run. The calorimeter, C , and all of its surroundings, shown in Fig. 1, were kept hot, day and night, by the steam-bath. Early in the morning the calorimeter was filled with hot distilled water and maintained at 98° C. all of the forenoon. After noon the heating current was started and the air regulated to hold the temperature constant at the same point. Only after a preliminary run of an hour or so, and when everything was running smoothly and constant, was the steam directed into one of the weighed flasks, and an experiment begun. A second and third experiment might follow, but not more than three runs were made during one day.

Variations.—All of the experiments were made at 98° C., as it was necessary to keep below the boiling point. Since the latter varied from

day to day over a range of nearly one degree, the corrections due to heat received by radiation, etc., varied by 100 per cent. Sometimes a series of experiments in each of which a large amount of water was evaporated, were made on one day; and a similar series of check experiments in each of which a small amount of water was evaporated were made on another day when all other conditions were as nearly the same as possible. At other times such check experiments were made at the beginning of the afternoon, and immediately followed by the experiments with larger heats. Again, the check experiments followed the regular experiments. Thus in all respects were the check experiments performed under the same conditions as the others, except in the amounts of water evaporated.

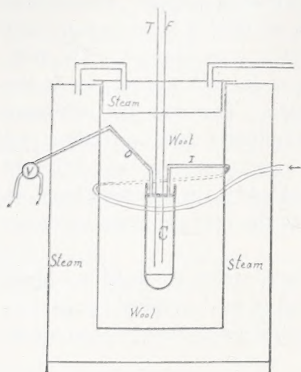


Fig. 1.

Calorimeter and steam jacket.

THE CALORIMETER.

The calorimeter consists of a thermos bottle, or vacuum walled jar, fitted with a copper lining which serves the double purpose of equalizing the temperature between the top and bottom and enabling the connecting tubes to be soldered in air tight. The internal arrangement is shown in Fig. 2.

The heating coil is made of about one ohm of manganin wire wound on a brass tube, and well insulated with silk and shellac, the whole being enclosed within a larger tube so that no water could come in direct contact with any part of the coil. The leads, LL' , were of heavy copper wire to reduce the amount of heat produced in them by the current, and which might then be conducted into the calorimeter. Potential leads, pp' , were soldered to the main leads close to the top of the calorimeter.

The glass tube, F , for filling and emptying the calorimeter, and the thermometer, T , were passed through snug fitting brass tubes which extended well into the water, thus completely sealing the joint. The rotary stirrer drew the water up through the tube on which the heating coil was wound. Friction was very small as it was mounted on glass bearings, and conduction of heat along the stirrer rod, S , was reduced to a minimum by making it of wood. The brass tubes, I and O , for

conveying the air current in and out were long and very thin-walled in order that the heat conduction might be as small as possible.

The incoming air was directed downward upon the surface of the water, while the outgoing stream of air and vapor passed through a coil in the water to warm it, if necessary, to the same temperature. Whatever small difference of temperature there may be between the incoming and outgoing air is measured by thermal junctions, Th , inserted into the tubes near the top of the calorimeter and corrections made therefor.

THE THERMOMETER.

The temperature of the water in the calorimeter was measured by the thermometer, T , which was graduated on the stem to hundredths of a degree, and could be read to thousandths. It was kept in the calorimeter all of the time and thus not subjected to great changes of temperature during the course of these experiments.

The readings of this thermometer do not enter into any computation, and the final result is independent of all temperature measurement. The thermometer serves merely as an indicator to enable the observer to keep the calorimeter at a constant temperature. The only use made of the actual reading is in determining the temperature at which the water was evaporated. The 98 degree mark was chosen as the constant temperature at which to hold the calorimeter. The upper fixed point of the thermometer was carefully determined by means of a regular hypsometer, the test being made in the same room and with the same stem correction as when the thermometer was used. The corrected value for the 98 degree mark was thus determined to be 98.07° C.

ELECTRIC HEATING.

The current for the heating coil was supplied from three sets of storage cells in parallel, and after the first two hours was remarkably steady, often maintaining five amperes without a change in the potentiometer for an hour. Both the current and the fall of potential over the heating

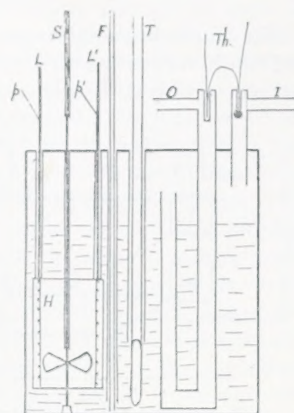


Fig. 2.

Interior of the calorimeter.

coil were measured in terms of a Weston normal cell, and the heat computed from the formula,

$$\text{Heat} = EITJ.$$

The electrical connections are shown in diagram by Fig. 3. The heating coil, H , is in series with a standard one-fourth ohm coil, C , the storage battery, a variable resistance, v , and an ammeter.

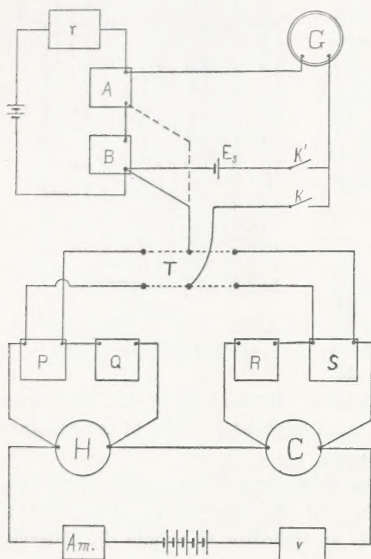


Fig. 3.

Electrical connections.

K' , and varying r ; then this fall of potential is balanced against that over P , using key K and adjusting Q .

In the check experiments, where the heating current is only half as large, the cell is balanced against both A and B , which are 10,000 ohms each, and then the fall of potential over P is balanced against that over A alone, as shown by the dotted connection.

The current is determined by measuring the fall of potential E' , over the standard resistance in the same way, by means of the double throw switch T , and its value is computed by the relation,

$$I = \frac{E'}{C} = \frac{R + S}{CS} E_s.$$

set at about the desired value and allowed to flow undisturbed. In parallel with H are two accurate high resistance boxes, P and Q . P remains set at 10,000 ohms, while Q is varied so as to maintain the fall of potential over P equal to the E.M.F. of the standard cell, E_s . Then the fall of potential over H , being the same as over P and Q together, is

$$E = \frac{P + Q}{P} E_s.$$

As the constant use of the standard cell would be liable to polarize it, this comparison is made by substitution, the fall of potential over AB in the auxiliary circuit ABr , being first balanced against the standard cell, using key

The total current is larger than this by the shunt current through R and S ; and for the same reason the current through the heating coil is smaller than the total current by the current through the shunt P and Q . These shunt currents are made equal by keeping P and S each set at 10,000 ohms, and thus the current through H is strictly equal to that through C . The resistances enter as ratios of coils in the same box and therefore require no temperature correction. The ratios were calibrated by comparison with standard coils from the Reichsanstalt. The exact values of E_s and C were determined by the Bureau of Standards.

Measurement of Time.—Each run was for a period of one hour, this interval being measured by a standard Riefler clock. The connection between clock and calorimeter was made by means of a high grade stop watch with a split seconds hand. Just on the hour by the clock, the time was recorded on the watch by stopping the lower half of the moving seconds hand. One minute later, with the watch held in the left hand and the right hand on the distributing valve, V , of the calorimeter, both hands were turned, one stopping the upper half of the seconds hand at the same time that the other turned the valve. Turning this valve ended one run and began the next. The exact time at which this was done could then be read from the watch to the nearest fifth of a second, and this was usually an even minute after the reading of the clock.

The Mechanical Equivalent of Heat.—The energy delivered to the calorimeter by the current is EIT joules. When it comes to translating this into heat units (calories) it is necessary to use the factor known as the mechanical equivalent of heat. And since the specific heat of water is not constant, but has a different value at each temperature, it is necessary to define precisely what is meant by the term "calorie." The unit used in this paper is the "mean calorie," that is, one per cent. of the heat that is required to warm one gram of pure water from 0° C. to 100° C.

The best direct determination of the mechanical equivalent of heat is doubtless that of Reynolds and Moorbey¹ in which they found

$$1 \text{ mean calorie} = 4.1836 \times 10^7 \text{ ergs.}^2$$

Probably the best determination of this constant by the electrical method is that of Callendar and Barnes³ who found

$$1 \text{ mean calorie} = 4.1849 \text{ joules,}^4$$

¹ Reynolds and Moorbey, Phil. Trans., Vol. 190 A, pp. 301-422, 1897.

² For a more complete discussion of this subject see paper by A. W. Smith, United States Weather Review, Vol. 35, pp. 458-463.

³ Callendar and Barnes, Phil. Trans., 1902.

⁴ Barnes, Proc. Roy. Soc. Lond., Vol. 82, p. 390, 1909.

provided the E.M.F. of their Clark cells be taken as 1.4333 volts at 15° C. This is equivalent⁴ to taking the E.M.F. of the standard Clark cell as 1.4330 at 15° C. or the Weston normal cell as 1.0187 volts at 20° C.

Since January 1, 1911, the E.M.F. of the Weston normal cell is taken as 1.0183 volts at 20° C., and all of my measurements are made in terms of this unit. Therefore, since the electrical determination of J includes E^2 , and any reduction in the number expressing the latter will reduce the former twice as much, the value for the mechanical equivalent of heat which should be used in connection with the value of 1.0183 for the Weston normal cell is

$$4.1849 \times \left(\frac{1.0183}{1.0187} \right)^2 = 4.1816.$$

The mean between these two values is 4.1826, and this is the value used in reducing my measurements to mean calories.

COLLECTING THE WATER.

The most difficult part of the work was the determination of the amount of water evaporated. While the value of the electric current can be accurately measured at any instant, the only way to find the corresponding rate of steam production is to collect the steam for an hour or so and weigh it. During this period, and for several hours preceding it, the rate of evaporation and the temperature of the calorimeter must be maintained constant, and this means continuous observation of the thermometer and adjustment of the air current. This is tedious, but necessary.

After leaving the calorimeter the stream of air and vapor passes through a two way valve, *V*, Fig. 1, by which it can be directed into either one of two sets of collecting tubes. In order that there should be no condensation of vapor in this valve or the connecting tubes they were enclosed in a box with an electric lamp which maintained the temperature at 130° C. The steam then passed into a half liter glass flask in a cold water-bath, where most of it was condensed. The remaining vapor, with the air, passed through three tubes containing H_2SO_4 where the water was all caught. (The incoming air was likewise dried by passing through H_2SO_4 .) The acid, of density 1.84, was very efficient in collecting the water, practically none of it getting through the first tube. As soon as the second tube began to catch water the first tube was refilled with fresh acid.

Weighing the Tubes.—The tubes and bulbs in which the water was caught were allowed to stand some time to assume room temperature.

They were then carefully wiped with a clean towel and weighed on a sensitive balance. All weighings were made with the aid of counterpoise consisting of a glass tube or bulb as nearly as possible like the one being weighed and likewise containing acid or water, as the case might be. All the tubes were kept closed except when on the balance; then the closing plug was a glass tube nearly sealed off. This allowed the pressure inside the tube to become the same as that outside, which is very important. The weighings were corrected for the buoyancy of the air, and to the weight of water thus determined was added the weight of the vapor filling the space in the calorimeter that had been occupied by the evaporated water.

RESULTS.

The results of these experiments are shown in Table I. Each value is computed from the results of two separate experiments. In the first column is shown the amount of water evaporated during one hour by a

TABLE I.

Heat of Evaporation of Water from a Smooth Surface at 98.07° C.

Water Evaporated (Grams).			Heat Supplied (Calories).			Calories Per Gram.
Large.	Small.	Difference.	Large.	Small.	Difference.	
37.3531	9.8858	27.4673	20,354	5,340	14,914	542.98
37.7645	9.1421	28.6224	20,379	4,888	15,491	541.23
37.7314	9.1132	28.6182	20,347	4,875	15,472	540.64
37.7146	9.1421	28.5725	20,375	4,888	15,487	542.03
37.5230	9.8858	27.6372	20,328	5,340	14,988	542.32
37.6916	9.8805	27.8111	20,379	5,320	15,059	541.48
37.6609	9.8805	27.7804	20,387	5,320	15,067	542.37
36.7130	9.3242	27.3888	19,816	4,974	14,842	542.15
36.6852	9.3242	27.3610	19,786	4,974	14,812	541.36
36.6826	9.3242	27.3584	19,784	4,974	14,810	541.34
36.5830	9.1421	27.4409	19,786	4,888	14,898	542.91
36.4116	9.1132	27.2984	19,689	4,875	14,814	542.68
36.4976	9.1421	27.3555	19,744	4,888	14,856	543.08
40.2116	8.6613	31.5504	21,686	4,582	17,104	542.12
36.8091	9.3242	27.4849	19,866	4,974	14,892	541.82
36.7000	8.6612	28.0388	19,750	4,582	15,168	540.96
37.3713	9.3242	28.0471	20,166	4,974	15,192	541.66
36.7925	8.9111	27.8814	19,878	4,774	15,104	541.73
36.1450	8.9735	27.1715	19,676	4,955	14,721	541.79
36.0249	8.9735	27.0514	19,612	4,955	14,657	541.68
Mean						541.93

current of about five amperes. In the second column is given the amount of water evaporated by about half as large a current during an hour on

another day when all the other conditions, as nearly as possible, were the same as on the first day. The difference between these amounts is given in the third column. The corresponding amounts of heat supplied to the calorimeter and their difference, are shown in the three succeeding columns.

The values in the last column are computed from these differences by formula (3), and each one is an independent determination of the heat of evaporation of water at 98.07° C. The mean of these values gives 541.93 mean calories per gram. At 100° C. this would be 1.23 less, or

$$L_{100} = 540.70 \text{ mean calories per gram.}$$

The probable error of this result, computed by the method of least squares from the variations among the individual determinations, is 0.025 per cent.

The work of Davis referred to above leads to the relation,

$$H_t = H_{100} + .3745 (t - 100) - .000990 (t - 100)^2,$$

where H_{100} denotes the unknown total heat (above 0° C.) of evaporation at 100° C., and H_t is its value at t° C. We can now write

$$H_t = 640.7 + .3745 (t - 100) - .000990 (t - 100)^2,$$

which gives the value of the total heat of evaporation, expressed in mean calories, at any desired temperature t° C.

TABLE II.

Heat of Evaporation of Water when Boiling at 100° C.

Water Evaporated (Grams).			Heat Supplied (Cals.).			Calories per Gram.	Temp.	Heat of Evaporation at 100° C.
Large.	Small.	Diff.	Large.	Small.	Diff.			
36.6929	8.9916	27.7013	19,894	4,979	14,915	538.4	99.30	538.0
36.7179	8.9693	27.8486	19,905	4,946	14,959	537.7	99.30	537.3
36.6019	8.4318	27.5692	19,440	4,680	14,760	535.4	99.64	535.2
35.7199	8.4311	27.2888	19,316	4,680	14,636	536.4	99.66	536.2
Mean								536.7

While this result is about one per cent. larger than the old value, it is not as much larger as might have been expected if we are to believe the current statements that steam often carries several per cent. of moisture. Nor is there much chance of any constant error due to this method, or the apparatus, as a number of experiments were made in precisely the same way as those described above except that the air

current was much reduced. This allowed the water to boil, while the air current was only enough to keep the steam moving in the right direction and to prevent its working back and condensing in the incoming air tube. The data from these experiments are shown in Table II., and the final result, reduced to 100° C., gives 536.7 mean calories per gram. This shows that the old value can be obtained with this apparatus by using the old method and allowing the water to boil. By merely checking the boiling and causing the evaporation to take place from the smooth surface of the water the heat of evaporation is increased by 4 calories per gram. This is probably due to the fact that the steam leaving the calorimeter in the latter case is all vapor, while in the former case some liquid is also carried away and counted as vapor.

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SOME THERMODYNAMIC PROPERTIES OF AIR AND OF CARBON DIOXIDE.

By A. G. WORTHING.

I. INTRODUCTION.

GAY-LUSSAC¹ was the first to investigate the question as to whether or not the internal energy of a mass of gas is a function of its volume. He was not able to conclude that the internal energy was a function of the volume. On Gay-Lussac's work R. Mayer² based his computations for the mechanical equivalent of heat. Joule³ with somewhat greater care and with a modified method came to the same conclusion. In each of these experiments, the gas under consideration was allowed to expand freely, that is without the performance of external work and without the addition or subtraction of heat. This latter condition was only imperfectly realized. The question as to whether or not the internal energy of the gas was a function of the volume depended directly on whether or not the freely expanding mass of gas taken as a whole suffered any change in temperature. The ratio of such a change in temperature to the change in pressure for small changes in pressure is called the free-expansion effect. Later repetitions of Joule's experiment by Regnault⁴ and by Hirn⁵ led to the same result. Cazin⁷ about 1870 sought to do away with errors due to heating. He noted the variations with time of a fluctuating liquid pressure gauge one side of which was connected to the chamber containing the gas under experimentation. Cazin concluded that the internal energy of a gas was a function of its volume and obtained values therefor which will be noted later. Due to the use of extended extrapolations and the presence of heating effects in the stop-cock separating his two chambers initially, the results are of doubtful significance. The writer is in receipt of a letter from Professor R. A. Millikan, in which he states that he has tried a method differing

from Cazin's in that the fluctuations of the liquid in the pressure gauge were eliminated by a null method. He was not able, however, to eliminate the heating effects at the stop-cock.

The method first successfully employed was due to Joule and Thomson⁹ (Lord Kelvin). Their celebrated porous plug experiments gave consistent results, which only needed corrections for external work done by the gas in the expansion in order to show the dependency of the internal energy of the gas upon the volume. The physical quantity (μ) determined by them was the ratio of the change in temperature to the change in pressure for small changes of pressures occurring as the gas passed through the porous plug. This quantity has since received the name Joule-Thomson effect or Joule-Kelvin effect. For moderate pressures they found μ independent of the pressure and dependent on the temperature as shown in (1),

$$(1) \quad \mu = A \theta^2.$$

Rose-Innes,¹⁰ D. Berthelot¹¹ and Buckingham¹² have given other equations for representing the same effect.

Natanson,¹³ working with CO₂ under higher pressures, found a noticeable though small diminution in the Joule-Kelvin effect for increased pressures. Kester,¹⁴ working with CO₂ under still greater pressures, did not find this change due to the change in pressure. Rudge¹⁵ has recently made some rough determinations for CO₂ with a modified method, in which the gas escapes from a pierced bulb in a calorimeter, through a long piece of narrow tubing. His results as a whole are in agreement with those of the previous experiments mentioned. Recently Dalton,¹⁶ working with air, has found an effect similar to that found by Natanson for CO₂. Witkowski,¹⁷ having in view the applications to liquid air machines, applied thermodynamic formulæ to a great many experimentally determined results. He computed by graphical methods a series of curves which were drawn on a pressure-temperature diagram, the slopes of which at any point give directly for that point the Joule-Kelvin and the free-expansion effects. Many steps are involved in reaching the final results, and confirmation is needed for this highly important work. Searle,⁸ making use of Van der Waal's equation and assuming the constancy of the isometric heat capacity, computed for CO₂ the change in temperature for the gas expanding from a pressure of 10 atmos. to 5 atmos. Some of the results of these investigations will be noted later.

The present paper is the immediate outcome of an attempt to better comprehend the dependency of the ratio of the two heat capacities of a substance γ on its pressure and temperature. It has led to the develop-

ment of a certain thermodynamical equation which relates the ratio γ to the free-expansion effect. This together with another well-known relation for the Joule-Kelvin effect has been used in computing these effects for air and CO_2 . There existed what seemed to be satisfactory data for air. An experimental study of γ for CO_2 was undertaken in this connection to complete what seemed necessary data for that gas.

II. DERIVATION OF FORMULÆ RELATING THE RATIO γ TO THE FREE-EXPANSION AND THE JOULE-KELVIN EFFECTS.

For convenience there is given in Table I. the symbols and the units of some of the quantities used in this discussion.

Definitions of N. V. Unit, T. N. V. Unit, μ and η .—The "normal volume unit" (N. V. unit) of a substance is defined by K. Onnes* as the volume actually occupied at 0°C . by one gram-molecule of the substance when under a pressure of one atmosphere. The "theoretical normal volume unit" (T. N. V. unit) is defined as the volume that would

TABLE I.

Symbols and units of some of the quantities used.

Quantity.	Symbol.	Unit.
Pressure,	p	atmosphere.
Specific volume,	v	$\frac{\text{N. V. unit}}{\text{gr. mol.}}$ $\frac{\text{T. N. V. unit}}{\text{gr. mol.}}$
Temperature,	T	degree Centigrade.
Thermodynamic temperature,	θ	degree Kelvin.
Time,	t	second.
Reduced pressure,	π	critical pressure.
Reduced temperature,	π	critical temperature.
Reduced specific volume,	π	critical specific volume.
Quantity of heat,	Q	atmo. $\times$ N. V. unit.
Specific internal energy,	e	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.}}$
Isopiestic heat capacity,	$(C)_p$	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}$ $\frac{\text{calories}}{\text{gr.} \times \text{deg.}}$
Isometric heat capacity,	$(C)_v$	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}$ $\frac{\text{calories}}{\text{gr.} \times \text{deg.}}$
Ratio of the two heat capacities,	γ	
Internal work in infinitesimal, reversible, isothermal expansions,	ΔW_1	atmo. $\times$ N. V. unit.
External work in infinitesimal, reversible, isothermal expansions,	ΔW_2	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{deg.}}$
Free-expansion effect,	η	$\frac{\text{deg.}}{\text{atmo.}}$
Joule-Kelvin effect,	μ	$\frac{\text{deg.}}{\text{atmo.}}$

be occupied at 0° C. by one gram-molecule of the substance under a pressure of 1 atmosphere if the gas obeyed Boyle's Law. It is assumed that the value of the product $p\bar{v}$ in such a case is the value of $p\bar{v}$ which may be obtained by extrapolation to zero pressure when considering the behavior of the actual gas. The measuring of volume in such units requires that C_p , C_v and ϵ be expressed in the units given in Table I. instead of the common units of cal./(gr. $\times$ deg.) and cal./gram. The free-expansion effect, η , of a substance, as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance into a vacuum. Mathematically it is

$$(2) \quad \eta = (\partial\theta/\partial p)_{\epsilon}.$$

The Joule-Kelvin effect, μ , as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance through an orifice or a porous plug from one maintained pressure to another maintained pressure. Mathematically it is

$$(3) \quad \mu = (\partial\theta/\partial p)_{\epsilon+p\bar{v}}.$$

For the sake of accuracy in the theoretical discussions, it has been necessary to express temperature in the units of the thermodynamic scale. For other purposes it makes but little difference in the present work whether temperatures are measured in this scale or in the more common

centigrade scale. In the adapting of experimental data, the writer has assumed that the degree Kelvin and the degree centigrade were equal.

Derivation of Equation Relating η and γ .—The equation relating η , the free-expansion effect, to γ , the ratio of the two heat capacities may be readily obtained. Consider changes in ϵ , the internal energy of

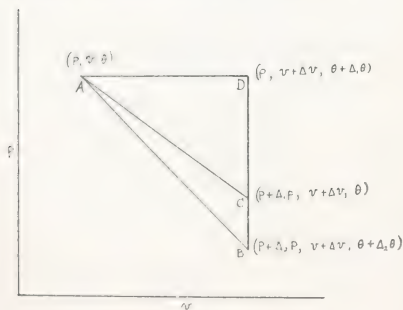


Fig. 1.

the substance under consideration, for transformations indicated in Fig. 1. Let the change represented by the straight line AB be an infinitesimal transformation in which there is no change in the specific internal energy ϵ ,

an infinitesimal free-expansion. Let the changes represented by AD , DB and AC be respectively infinitesimal isopiestic, isometric and isothermal transformations. Due to carrying the substance around the cycle $ABDA$, no resultant change occurs in ϵ . Consequently the individual changes in ϵ occurring in the individual transformation making up the cycle must sum up to zero. Moreover, since there are no changes in ϵ along AB , the changes in ϵ in passing along BD and DA must sum up to zero. Hence

$$(4) \quad C_v(\Delta_1\theta - \Delta_2\theta) - C_p\Delta_1\theta + p\Delta v = 0.$$

Since the transformations are infinitesimal, we have

$$(5) \quad \Delta_1\theta = \frac{\Delta_1\theta}{\Delta v} \Delta v = \left(\frac{\partial\theta}{\partial v}\right)_p \Delta v,$$

and

$$(6) \quad \begin{aligned} \Delta_2\theta &= \frac{\Delta\theta}{\Delta_2p} \frac{\Delta_2p}{\Delta v} \Delta v = \left(\frac{\partial\theta}{\partial p}\right)_\epsilon \left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta v \\ &= \eta \left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta v. \end{aligned}$$

Eliminating $\Delta_1\theta$, $\Delta_2\theta$ and Δv from (4), we have

$$(7) \quad (C_p - C_v) \left(\frac{\partial\theta}{\partial v}\right)_p - p + \eta C_v \left(\frac{\partial p}{\partial v}\right)_\epsilon = 0.$$

An expression for $(\partial p/\partial v)_\epsilon$ may be obtained as follows. For all transformations we have

$$(8) \quad dp = \left(\frac{\partial p}{\partial\theta}\right)_v d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta dv.$$

Hence

$$(9) \quad 1 = \left(\frac{\partial p}{\partial\theta}\right)_v \frac{d\theta}{dp} + \left(\frac{\partial p}{\partial v}\right)_\theta \frac{dv}{dp}.$$

For a free-expansion (9) becomes

$$(10) \quad 1 = \left(\frac{\partial p}{\partial\theta}\right)_v \left(\frac{\partial\theta}{\partial p}\right)_\epsilon + \left(\frac{\partial p}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial p}\right)_\epsilon,$$

or

$$(11) \quad \left(\frac{\partial p}{\partial v}\right)_\epsilon = \frac{\left(\frac{\partial p}{\partial v}\right)_\theta}{1 - \eta \left(\frac{\partial p}{\partial\theta}\right)_v}.$$

The elimination of $(\partial p/\partial v)_e$ from (7) and (11) gives

$$(12) \quad \gamma = \frac{C_p}{C_v} = 1 + \frac{p}{C_v} \left(\frac{\partial v}{\partial \theta} \right)_p + \frac{\eta \left(\frac{\partial p}{\partial \theta} \right)_v}{1 - \eta \left(\frac{\partial p}{\partial \theta} \right)_v}.$$

The expressions for γ usually derived in text-books on physics are equivalent to the first two terms of the right-hand member of (12). By means of it and of certain assumptions regarding the application of the kinetic theory of gases, it is shown that for cases where such assumptions are realized the limiting values of γ are 1 and 1.29. Equation (12), however, is a perfectly general expression. It reduces to the more common expression for small pressures where $(\partial p/\partial \theta)_v$ is small and the term containing η may be disregarded. The writer has not seen elsewhere any expression similar to (12).

Equation (12), when combined with the following well-known relation deduced in texts on thermodynamics

$$(13) \quad C_p - C_v = \theta \left(\frac{\partial p}{\partial \theta} \right)_v \left(\frac{\partial v}{\partial \theta} \right)_p,$$

gives

$$(14) \quad \eta = \frac{\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p}{\frac{\gamma}{\gamma - 1} \theta \left(\frac{\partial p}{\partial \theta} \right)_v - p} \left(\frac{\partial \theta}{\partial p} \right)_v.$$

Expression of μ as a function of γ .—In texts on thermodynamics the following equation for the Joule-Kelvin effect is derived:

$$(15) \quad \mu = \frac{\theta \left(\frac{\partial v}{\partial \theta} \right)_p - v}{C_p}.$$

Equations (13) and (15) lead directly to the following

$$(16) \quad \mu = \frac{\gamma - 1}{\gamma} \frac{\theta - v \left(\frac{\partial \theta}{\partial v} \right)_p}{\theta \left(\frac{\partial p}{\partial \theta} \right)_v}.$$

Equations (14) and (16) are the two relations, the application of which form certain of the main subdivisions of this paper.

III. THE FREE-EXPANSION AND JOULE-KELVIN EFFECTS IN AIR.

Inspection of Available Data.—In order to apply equations (14) and (16), there are needed experimental data regarding γ , the interrelations of p , v , θ and their partial derivatives $(\partial p/\partial \theta)_v$ and $(\partial v/\partial \theta)_p$. γ for air may be obtained from data by Witkowski,²⁶ by Koch,²⁴ or from data by Joly²⁷ and Lussana.²⁸ Witkowski first computed C_p and C_v and then γ . C_p was obtained from the relation

$$(17) \quad \left(\frac{\partial C_p}{\partial p} \right)_\theta = -v \left(\frac{\partial v}{\partial \theta} \right)_p.$$

C_v was obtained by means of (13). Values of γ were then computed for various temperatures ranging from 0°C. to -140°C. , and for pressures up to about 130 atmospheres. Later by Kundt's velocity of sound method, he measured γ directly under pressures up to 100 atmospheres and at 0°C. and -78.5°C. These results, though noticeably higher, agree quite well with the computed results, as may be seen by an inspection of Table II. Koch's results were likewise obtained by Kundt's velocity of sound method. In his experiments the pressure varied from 1 to 200 atmospheres. The temperatures were 0°C. and -79.3°C. His results agree well with Witkowski's. Joly determined C_v for air by means of his well-known, differential, steam-calorimeter method for various temperature intervals all above 0°C. and for pressures up to about 100 atmospheres. Average values of C_p for air were determined by Lussana for various intervals of temperature between 0°C. and 200°C. and for various pressures up to 100 atmospheres. These values of C_v and C_p and the values of $(\partial v/\partial \theta)_p$ and $(\partial p/\partial \theta)_v$ obtained by Amagat from his experiments on the compressibility of air, have been shown by Amagat to be quite inconsistent with one another. Data by Joly and Lussana have therefore not been relied upon in this work. The writer has seen only an abstract of Witkowski's paper in which the Kundt method of measuring γ was detailed. For the above reasons and for the added reason that the data by Koch seemed to have been obtained with great care, Koch's data have been used in the following computations. The values obtained from Koch's paper are to be found in Table II., column 7.

For the determination of the interrelations of p , v , and θ and the partial derivatives $(\partial v/\partial \theta)_p$ and $(\partial p/\partial \theta)_v$, there exist the works of Amagat,²⁹ Witkowski¹⁷ and Koch²⁴. Amagat's data relate to temperatures above 0°C. and can not be used in connection with the data on γ selected. Witkowski's results on the compressibility of air cover the range of temperatures and pressures of the γ data selected. Moreover, the values of the product $p v$ as a function of p at 0°C. and -78.5°C. have been

fairly well verified by Koch. Witkowski's data on the compressibility of air have therefore been made use of.

Method of Handling p, v, θ data.—In applying equations (14) and (16), $(\partial v / \partial \theta)_p$ and $(\partial p / \partial \theta)_v$ do not merely appear by themselves but also in the expressions $v(\partial \theta / \partial v)_p$ and $\theta(\partial p / \partial \theta)_v$. The values for these expressions were obtained as follows: Consider

$$(18) \quad (pv)_\theta = f(p).$$

The derivation of (18) with respect to p gives on rearranging

$$(19) \quad \left(\frac{\partial p}{\partial v} \right)_\theta = - \frac{p}{v - f'(p)}.$$

Likewise we may consider

$$(20) \quad (v)_p = F(\theta).$$

Whence

$$(21) \quad \left(\frac{\partial v}{\partial \theta} \right)_p = F'(\theta),$$

and

$$(22) \quad v \left(\frac{\partial \theta}{\partial v} \right)_p = \frac{F(\theta)}{F'(\theta)}.$$

Since

$$(23) \quad \left(\frac{\partial p}{\partial \theta} \right)_v = - \left(\frac{\partial p}{\partial v} \right)_\theta \left(\frac{\partial v}{\partial \theta} \right)_p,$$

$$(24) \quad \theta \left(\frac{\partial p}{\partial \theta} \right)_v = \frac{p \theta F'(\theta)}{v - f'(p)}.$$

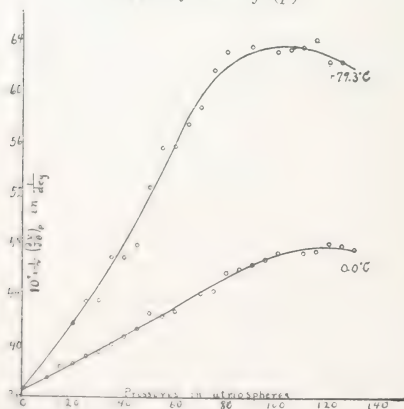


Fig. 2.

Variation of $\frac{1}{v} \left(\frac{\partial v}{\partial \theta} \right)_p$ with pressure for air.

For air at various pressures and at $0^{\circ}\text{C}.$ and $-79.3^{\circ}\text{C}.$, $f'(p)$ and $F'(\theta)$ were obtained from Witkowski's data by graphical means. The individual values of the reciprocals of $v(\partial\theta/\partial v)_p$, which were obtained together with the smoothed curves are shown in Fig. 2. The values used were taken from these curves.

Results from Data by Witkowski and Kock.—Certain data and computations leading to the values of μ and η are included in Table II. The

TABLE II.

Computations for μ and η of air using data obtained by Witkowski and by Kock. Air at $0^{\circ}\text{C}.$

t	p	$\log\left[-\left(\frac{\partial p}{\partial v}\right)_{\theta}\right]$	$\log\left(\frac{v}{v_0}\right)_t$	$\mu = \tau\left(\frac{v_0}{v}\right)_t$	$\mu\left(\frac{v_0}{v}\right)_t = p$	γ	κ	η	$\frac{\Delta W_1}{\Delta W_2}$
10	.9951	1.9997	4.5737	7.7	.23	1.435	.228	.259	.023
15	.9923	2.3519	.4026	11.4	.52	1.448	.227	.260	.035
20	.9897	2.6017	.2824	15.0	.92	1.460	.226	.259	.046
25	.9869	2.7958	.1906	18.6	1.48	1.472	.225	.265	.059
30	.9842	2.9546	.1160	22.0	2.13	1.483	.223	.263	.071
40	.9793	3.2057	.0005	28.7	3.92	1.508	.220	.270	.090
50	.9754	3.4010	5.9134	35.1	6.35	1.533	.217	.275	.127
60	.9723	3.5614	.8440	41.2	9.48	1.557	.212	.278	.158
70	.9701	3.6969	.7881	47.0	13.46	1.582	.207	.281	.192
80	.9688	3.8160	.7392	52.5	18.10	1.603	.201	.279	.226
90	.9681	3.9212	.6984	57.7	23.8	1.625	.195	.278	.264
100	.9681	4.0155	.6598	61.3	29.4	1.645	.186	.270	.294
110	.9690	4.1034	.6244	64.0	36.0	1.663	.175	.263	.327
120	.9710	4.1838	.5882	64.5	41.6	1.682	.162	.253	.347
130	.9738	4.2602	.5530	63.6	47.7	1.700	.147	.243	.367

Air at $-79.3^{\circ}\text{C}.$

1	.708	.1488	3.5643	.8		1.405	.230		
10	.690	2.1500	4.5866	15.1	.57	1.463	.452	.447	.057
15	.681	2.5022	.4236	22.6	1.34	1.495	.458	.463	.089
20	.672	2.7520	.3124	30.1	2.48	1.530	.464	.476	.124
25	.664	2.9459	.2299	37.4	4.05	1.567	.466	.489	.162
30	.655	3.1046	.1644	44.3	6.01	1.602	.462	.492	.200
40	.638	3.3541	.0664	56.9	11.04	1.681	.452	.487	.276
50	.620	3.5483	.0062	71.6	19.48	1.765	.447	.493	.390
60	.606	3.7071	5.9554	81.9	29.01	1.857	.424	.474	.483
70	.587	3.8499	.9209	93.1	44.4	1.950	.397	.457	.634
80	.573	3.9819	.8783	99.0	60.5	2.044	.360	.431	.756
90	.562	4.0981	.8340	102.3	75.8	2.125	.327	.397	.842
100	.554	4.2097	.7900	104.0	93.7	2.200	.293	.368	.937
110	.550	4.3122	.7478	104.4	112.5	2.290	.264	.344	1.023
120	.547	4.3998	.7072	104.3	128.0	2.370	.243	.324	1.067
130	.546	4.4804	.6683	103.7	143.0	2.460	.226	.308	1.100

μ is expressed in atmos. τ in $\frac{\text{N. units}}{\text{at. atm.}}$ and κ and η in $\frac{\text{atm.}}{\text{atm.}}$

value of the ice point for this table was taken as 273.2° K. The value used for the other and later computation was 273.1° K. The variations produced by not using the latter value throughout are inappreciable, hence Table II. has not been corrected in this respect. The computed free-expansion and Joule-Kelvin effects are indicated in Fig. 3 by open circles.

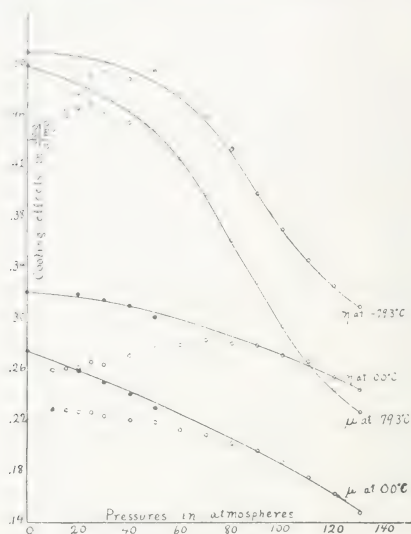


Fig. 3.

Variation with pressure of the free-expansion (η) and Joule-Kelvin (μ) effects in air at 0.0° C. and $= 79.3^{\circ}$ C.

Results based on

Witkowski's data. O
K. Onnes's equation. ●

K. Onnes's Equation.—The values in Fig. 3 indicated by circles with filled centers are obtained by using Kamerlingh Onnes's¹⁶ empirical equation representing the isothermals of air at 0° C., 20° C. and 99.4° C. for pressures up to about 50 atmospheres and Koch's data on γ . The equation given by Kamerlingh Onnes is

$$(25) \quad pv = A + \frac{B}{v} + \frac{C}{v^2},$$

where v is expressed in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, p in atmospheres, and A , B and C

are functions of θ , the individual values of A , B and C are as shown for the given temperatures in Table III.

TABLE III.

Constants for Kammerlingh Onnes's empirical equation (1a).

θ	A	B	C
0.0° C.	1.0006	-.0357440	.0329594
20.0° C.	1.0739	- .40495	.30178
99.4° C.	1.3647	+ .25057	.35669

Results from K. Onnes's Equation and Koch's Data.—The computations for μ and η , excepting those for zero pressure, differ in this case from those in which the p , v , θ relations were obtained from Witkowski's data in that $(\partial p/\partial v)_\theta$ was obtained in this case by differentiation. Table IV. indicates these results.

TABLE IV.

Computations for μ and η at $\theta = 0^\circ$ C. using Kammerlingh Onnes's equation at finite p and η data by Koch.

p	v	$\log \left[- \left(\frac{\partial v}{\partial p} \right)_\theta \right]$	$\log \left(\frac{\partial v}{\partial \theta} \right)_p$	$v - \tau \left(\frac{\partial v}{\partial \tau} \right)_p$	$\theta \left(\frac{\partial \theta}{\partial v} \right)_p - p$	γ	μ	η	$\frac{\Delta H_1}{\Delta H_2}$
0	1.0006	—	—	—	—	—	.273	.320	.000
10	.9952	2.0000	1.5759	8.9	.29	1.435	.262	.322	.029
20	.9902	2.6022	.2869	17.3	1.16	1.448	.258	.318	.058
30	.9859	2.9550	.1220	24.9	2.62	1.460	.249	.313	.087
40	.9822	3.2060	.0073	31.7	4.64	1.472	.239	.308	.116
50	.9790	3.4009	5.9199	37.7	7.18	1.483	.229	.300	.144

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{cc. mole}}$, and μ and η in $\frac{\text{deg.}}{\text{atm.}}$.

Values for μ and η at Zero Pressure.—The values for μ_0 and η_0 at $p = 0$ were obtained by a method indicated for μ_0 by J. P. Dalton.¹⁶ The method of obtaining η_0 is outlined briefly here. By means of (13), (14) may be rewritten as

$$(26) \quad \eta = \frac{\theta - p \left(\frac{\partial \theta}{\partial p} \right)_\theta}{C_v \left(\frac{\partial v}{\partial \theta} \right)_p - \theta}$$

By the direct processes of calculus and by the substitution of $v = \infty$, we get

$$(27) \quad \eta_0 = \frac{1}{C_v} \frac{\theta \left(\frac{\partial B}{\partial v} \right)}{A - \frac{\partial A}{\partial v}}$$

The analogous value for μ_0 obtained from (15) is

$$(28) \quad \mu_0 = \frac{\theta \frac{\partial B}{\partial \theta} - 2B}{C_{p0} A}.$$

The well established value of C_{p0} for air under low pressures is very closely $.2375 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$, or in the units consistent with those chosen for p and v in this paper $.01273 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.} \times \text{deg.}}$.

It is to be noticed that the two sets of values for μ and η included in Tables II. and IV. differ considerably, the greatest variations occurring with the smaller pressures. This is evidently due to the smallness of the quantities $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$. The entire differences result from very small but noticeable variations in corresponding values of $(\partial v/\partial\theta)_p$. This source of uncertainty is plainly much less effective at the higher pressures.

Results for μ at 0°C .—The value obtained for the Joule-Kelvin effect at zero pressure μ_0 at 0°C . from Kamerlingh Onnes's equation agrees very closely, as has been shown by J. P. Dalton, with the experimental value obtained by Joule and Kelvin and with his own experimental value. It also agrees very well with the computed value obtained by using Buckingham's equation in which he expressed in a single formula the results of all experimental Joule-Kelvin effects for various substances under moderate pressures, as a function of the temperature. Each of these values closely approximates $.273 \frac{\text{deg.}}{\text{atmo.}}$. This value has therefore been selected on the plot Fig. 3, as the starting point for the curve at 0°C . J. P. Dalton's experimental results for the porous plug expansion of air through a glass reduction-valve are very well represented by the equation,

$$(29) \quad T_1 - T_2 = .273(p_1 - 1) - .000208(p_1^2 - 1).$$

p_1 represents the initial pressure of the air, a quantity which in his experiments reached a pressure of 43 atmospheres. T_1 the initial temperature was 0°C . The final pressure was that of the atmosphere. T_2 represents the final temperature. The ratio $\frac{T_1 - T_2}{p_1 - 1}$, if plotted on Fig. 2 would start with the same initial value for μ_0 as chosen and would continue from there in a line lying approximately half way between the line $\mu = .273 \frac{\text{atmo.}}{\text{deg.}}$ and a line passing through the points determined by

Kamerlingh Onnes's equation and the γ data of Koch. When it is remembered that the results of Dalton represent effects from finite expansion of considerable magnitude and that the mean temperatures during such expansions are, for the higher pressures especially, noticeably less than 0° C., for which temperatures the Joule-Kelvin effect becomes greater, it will be seen that the deviation spoken of above is to be expected. Moreover, it may be readily shown that this deviation agrees in magnitude with what is obtained by some rather rough computations. For an initial pressure of 40 atmospheres, (29) gives for T_2 a value of -10.3° C. If now (1) may be taken as approximately true, and if it is further assumed that the value of μ for 0° C. and atmospheric pressure is $.273 \frac{\text{deg.}}{\text{atmo.}}$, it follows that the value of μ for -10.3° C. and atmospheric

pressure is $.294 \frac{\text{deg.}}{\text{atmo.}}$. The value for μ at 0° C. and 40 atmospheres, according to data based on Kamerlingh Onnes's equation, is $.239 \frac{\text{deg.}}{\text{atmo.}}$.

For air initially at 0° C. and 40 atmospheres, expanding through a valve as in J. P. Dalton's experiment to atmospheric pressure, an average value for μ might be expected which is near the mean of the extreme values given above. This computed average for μ , $.266 \frac{\text{deg.}}{\text{atmo.}}$, agrees

very well with the value to be obtained from (29), $.264 \frac{\text{deg.}}{\text{atmo.}}$. Because of these agreements, it has been assumed in drawing the curve for μ at 0° C. that the values computed with the aid of Kamerlingh Onnes's equation of state are correct. The general trend of these values are such as to show agreement with the values of μ obtained for the higher pressures using Witkowski's data. It might be expected that these latter values would not be far from the correct values, since here, as may be seen in Table II., small errors entering into $\theta - v(\partial\theta/\partial v)_p$ would cause but small errors in the computed results for μ . Hence the further continuance of the curve. The curve for μ at 0° C. is well represented by (30).

$$(30) \quad \mu_{T=0} = .273 - .00076p + .0000012p^2.$$

Results for μ at -79.3° C.—In drawing the curve for μ at -79.3° C., the value given by Buckingham's equation was selected as being the most probable value for μ at zero pressure. This value of $.498 \frac{\text{deg.}}{\text{atmo.}}$ was found to agree very well with the value $.486 \frac{\text{deg.}}{\text{atmo.}}$ for -78.5°

which was obtained by using as before, equations similar to (25) and Witkowski's experimental value of C_p $.2375 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ or $.01273 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$. The equations used here however were of the type

$$(31) \quad pv = A + B'v.$$

A and B have the values indicated in Table V. at the stated temperatures

TABLE V.

Constants for equation (31).

T	A	B
0.0° C.	1.0006	-.000574
- 78.5	.7130	-.001193
-103.5	.6214	-.001473

when as before p is expressed in atmospheres and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$. The values of A and B relating to 0° C. have been given by Kamerlingh Onnes. The remaining values of A were determined on the supposition that at zero pressure air rigorously obeys the perfect gas law. The remaining values for B were determined with the additional supposition that Witkowski's data on the values of v for air at - 78.5° C. and - 103.5° C. for a pressure of 20 atmospheres are correct. These values are respectively .03389 and .02848 $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$.

Results for η at 0° C.—In drawing the curve for the free-expansion effect η of air at 0° C., preference was given at small pressures to the values computed with the aid of Kamerlingh Onnes's equation and constants, because they had given very nearly the correct results for the Joule-Kelvin effect at the same temperature and pressure. It is, of course, to be borne in mind that, even if an equation of state should indicate correct values for the Joule-Kelvin effect for any pressure and temperature, the computed free-expansion effects as determined by that equation of state might deviate far from the true values. If, however, in addition to leading to the correct Joule-Kelvin effects, the equation correctly represents the isothermals, then as has been shown by Bakker,³⁰ the equation will lead to correct free-expansion effects. As in connection with the Joule-Kelvin effect and for a similar reason, we may expect that the computed free-expansion effects based on Witkowski's data, in the case of high pressures, will not deviate far from the true values.

Here $\theta(\partial p/\partial \theta)_v - p$ is the term which practically determines the accuracy of the computed results. The writer knows of no direct determinations of η which might be used here. The curve for η at 0° C. is well represented by (32).

$$(32) \quad \eta_{100} = .320 - .00018p - .0000032p^2.$$

Results for η at -79.3° C.—In drawing the curve for the free-expansion effect η at -79.3° C., the value for zero pressure was chosen as follows: The value computed with the aid of equation (31) and the accompanying constants for zero pressure and -78.5° C. was $.496 \frac{\text{deg.}}{\text{atmo.}}$. Since the Joule-Kelvin effect for zero pressure and -78.5° C. computed from the same data differed by $.012 \frac{\text{deg.}}{\text{atmo.}}$ from the value given by Buckingham's equation for -79.3° C., and since the variations of μ and η with temperature seem to be about the same, as the general trend of the curves drawn indicate, it was assumed, that the value for η at -79.3° C. was higher than the computed value at -78.5° C. by $.012 \frac{\text{deg.}}{\text{atmo.}}$, making the value selected $.508 \frac{\text{deg.}}{\text{atmo.}}$.

Agreement with Witkowski's Results.—There has been mentioned the work of Witkowski.¹⁷ He started with a number of experimentally determined relations between p , v and θ , and with the experimental conclusion that C_p for air at 1 atmosphere is independent of the temperature, computed isenthalpic and isenergetic curves for air embracing a region from 0° C. to -140° C. and from zero pressure to 130 atmospheres. Graphical methods were largely used. The slopes of these curves give directly the Joule-Kelvin and the free-expansion effects. The writer has included in Table VI. a number of values for μ and η thus obtained together with the corresponding values from the present work. Excepting for the lower pressures, the agreement is good. As has been previously suggested, the variations here are undoubtedly largely due to the smallness of the corresponding values for $\theta - v(\partial \theta/\partial v)_p$ and $\theta(\partial p/\partial \theta)_v - p$. Witkowski himself ascribed the variation of his results from those of Joule and Kelvin to the uncertainties entering into his graphical calculations.

Internal Work of Expansion.—It is of considerable interest in this connection to consider the relative magnitudes of the effects of the internal forces, intramolecular as well as intermolecular, which give rise to the free-expansion and to a large extent to the Joule-Kelvin effects. This

TABLE VI.

Corresponding values of μ and η according to Witkowski and to Worthing.

T in °C.	Values of μ in deg. atmo.			T in °C.	Values of η in deg. atmo.		
	β in Atmos.	(Witkowski)	(Worthing.)		β in Atmos.	(Witkowski.)	(Worthing.)
0.0	40	.20	.242	0.0	50	.23	.303
	70	.23	.215		84	.265	.282
	113	.175	.175		121	.252	.252
	0	.515	.498		19	.491	.505
-79.3	15	.496	.490	-79.3	38	.509	.496
	30	.476	.476		55	.500	.480
	43	.468	.460		71	.468	.452
	57	.448	.430		88	.424	.403
	69	.400	.397		104	.358	.358
	83	.365	.349		122	.323	.322
	97	.308	.303				
	112	.248	.260				
	130	.222	.226				

may best be done by determining the ratio of the work done against these internal forces ΔW_1 to that done against external forces ΔW_2 when a gas undergoes an infinitesimal, reversible, isothermal expansion. The internal work for such an expansion is evidently equal to the change in internal energy, which in turn is equal to the heat, measured in appropriate units, which must be added to the substance following the free-expansion from the initial to the final volume to bring it without changing the volume to the initial temperature.

$$(33) \quad \Delta W_1 = (\Delta \epsilon)_\theta = -C_v \eta (\Delta p)_\epsilon = -C_v \eta \left(\frac{\partial p}{\partial v} \right)_\epsilon \Delta v.$$

With the aid of (11), (12) and (13), there follows

$$(34) \quad \Delta W_1 = \left(\frac{\partial \epsilon}{\partial v} \right)_\theta \Delta v = - \frac{C_v \eta \left(\frac{\partial p}{\partial v} \right)_\theta}{1 - \eta \left(\frac{\partial p}{\partial \theta} \right)_v} \Delta v = \left[\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p \right] \Delta v.$$

The desired ratio of the internal work to the external work is given by

$$(35) \quad \frac{\Delta W_1}{\Delta W_2} = \frac{\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p}{p}.$$

This relation is true for all infinitesimal, reversible expansions in which the accompanying changes in p are infinitesimal. Values for $\Delta W_1/\Delta W_2$

for air have been computed and are to be found in the last columns of Tables II, and IV. The results have been platted in Fig. 4. In Fig. 4 only those points have been platted for which the corresponding computed values of μ and η were found to fall closely on the platted curves of Fig. 3. What has been noted previously regarding the uncertainties in $\theta(\partial p/\partial \theta)_s = p$ at low pressures, applies equally here. The changes in $\Delta W_1/\Delta W_2$ with pressure and with temperature are very evident, the ratio for the lower temperature and the higher pressures being greater than unity.

Conclusions Regarding η , μ and $\Delta W_1/\Delta W_2$ of Air.—

The plats show that in air for the region considered:

1. The free-expansion effect η is greater than the Joule-Kelvin effect μ for the same pressure and temperature.

2. The absolute difference between η and μ for the same pressure and temperature increases with increasing pressure.

3. Both η and μ are greater for the lower temperature than for the higher temperature.

4. Both η and μ beginning with low pressures, decrease with increasing pressures, the rate of decrease being the greater, the greater the pressure.

5. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\Delta W_1/\Delta W_2$ is greater at -79.5°C. for a given pressure than at 0°C.

6. The ratio $\Delta W_1/\Delta W_2$ starts with zero values at zero pressure and increases with pressure, and in the case of the lower temperature, reaches a value greater than unity.

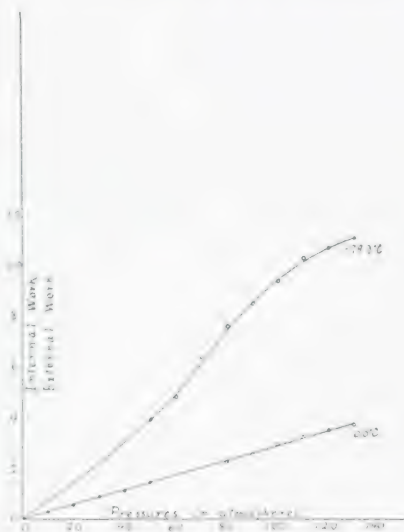


Fig. 4.

Variation with pressure of internal work in air for infinitesimal, reversible, isothermal expansions.

Results based on

Without data $\circ$ K. Onnes's equation $\bullet$

IV. THE DETERMINATION OF γ FOR CO_2 AS A FUNCTION OF THE PRESSURE AND THE TEMPERATURE.

Consideration of Existing Data.—There exist many determinations of γ for CO_2 under atmospheric pressure. There exist for pressures considerably greater, so far as the writer knows, only the computations of Amagat,¹³ in which he combines the determinations of C_v made by Joly³² with his own determinations of the interrelations of p , v and θ . His own work enabled him to determine $\theta(\partial p/\partial \theta)_v(\partial v/\partial \theta)_p$ for the gas at any desired pressure and temperature. By the application of (13), C_p and then γ were determined; first at varying pressures for a density of the CO_2 of .124 gr. cm.³, then at varying pressures for a temperature of 50° C. He obtained various values for γ which showed that quantity to increase noticeably with increasing pressure and with decreasing temperature. For a temperature of 50° C. and a pressure of 100 atmospheres, he found γ to be 4.633. Unfortunately the results are such that it is impossible to check them by comparing them with other determined values at one atmosphere.

At about the same time there appeared papers by Lussana³³ on the values of C_p for CO_2 at about the same pressures and temperatures. Evidently his results might be combined with Amagat's, C_v determined and then γ ; or his results might be combined with Joly's directly and γ thus determined. The writer has attempted the latter. It has been necessary to plot the given values of C_p and C_v in order to get values for C_p and C_v under the same conditions. Table VII. includes the results

TABLE VII.

γ for CO_2 from data by Joly and by Lussana.

t°	30°			50°			80°		
	C_p	C_v	γ	C_p	C_v	γ	C_p	C_v	γ
10	.297	.169	1.76	.259	.169	1.53	.250	.168	1.49
20	.301	.173	1.75	.263	.172	1.53	.253	.171	1.48
30	.318	.179	1.72	.268	.177	1.52	.258	.175	1.48
40	.318	.184	1.73	.276	.182	1.52	.264	.180	1.47

p is expressed in atmospheres. C_p and C_v are expressed in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of such computations. Joly's conclusion, that for densities less than .124 gr./cm.³ C_v for CO_2 is practically independent of the temperature, was assumed as correct. There are only a few values which may be compared with those mentioned above as having been obtained by Amagat. There is but very little agreement between the two sets of

determinations. Moreover the variations of γ in Table VII. are such as would indicate values of γ under atmospheric pressure which are very different from the generally accepted values. There is evident need of further determinations of γ for CO_2 for various pressures and temperatures.

Methods of Measuring γ for Gases under High Pressures.—There are several methods of determining γ which are practicable when applied to a gas under high pressures. There are (1) the thermodynamic method used by Witkowski as described briefly in an earlier part of the present paper; (2) the separate determination of C_p and C_v ; (3) the determination of C_p and the consequent computation of C_v by equation (13); (4) the determination of C_v and the consequent determination of C_p by equation (13); (5) the method of Jamin and Richard¹⁶ in which the isopiestic and isometric changes in temperature of a gas heated by a wire carrying an electric current is measured; (6) the method of Assmann,¹⁷ in which there is observed the period of vibration of a system in a closed glass tube composed of a mass of the gas separated into two parts by means of a column of mercury; (7) the velocity of sound method; (8) the method of Lummer and Pringsheim¹⁸ so modified as to apply to gases far removed from the state of perfect gas; and (9) the method of Maneuvrier,¹⁷ a null method based on the same fundamental principles as the method commonly called after Clement and Desormes.

Reasons for Choosing the Method Selected.—The thermodynamic method of Witkowski might be applied to the data given by Amagat for CO_2 . There would be required in addition however the variations of C_p or C_v with temperature at a given pressure such as atmospheric. Such determinations as these have been made but there is a great lack of consistency in the data. It has not seemed desirable to make use of this method in the present case. The next three methods necessitate the measurement of C_p , C_v or both for various pressures and temperatures. These are very difficult undertakings. Moreover, as they have already been measured by Joly and Lussana as noted above, and with very probable, serious errors as is suggested by Table VII., none of these three methods has been used in the present work. Jamin and Richard's method would undoubtedly be hard to realize under high pressure, especially in the carrying out of an isopiestic heating. Assmann's method might well yield good results, when all allowances are made for disturbing factors. The velocity of sound method has been used by Witkowski and by Koch for air with fair agreement of results with each other and with the former's results by the thermodynamic method. This method has been criticized by J. W. Capstick,¹⁹ and by J. H. Jeans,²⁰ on account of a lag in the

adjustment of the intermolecular and intramolecular energies of a gas on the passage of a sound wave through the gas. In Chapter XVI. of his "The Dynamical Theory of Gases" he concluded that any such lag in adjustment, provided that a certain supposition is true, "is in every way imperceptible." The method of Maneuvrier seemed free from this serious objection. It has been used. Practically, in Maneuvrier's method the compressions are no more reversible than those in sound experiments. Time, however, is given in this method for the practical balancing of the intramolecular and the intermolecular energies before actual measurements are made. The apparatus which was constructed for this work has been so designed as to make possible measurements according to a modification of Lummer and Pringsheim's method. However, time has not been found available for the perfection of this method, and consequently no measurements of that kind have been made.

Maneuverier Method.—The method of Maneuvrier is based on a theorem due to Reech,⁴⁰ which is applicable to any substance whatever. A simple derivation of the equation expressing this theorem follows. Let AB , AC , AD and DB , Fig. 1, represent in this instance respectively infinitesimal reversible adiabatic, isothermal, isopiestic and isometric changes. Consider the change in internal energy which takes place when a substance is carried around the cycle $ADBA$. We have then

$$(36) \quad (C_p \Delta_1 \theta - p \Delta v) + C_v (\Delta_2 \theta - \Delta_1 \theta) + p \Delta v = 0.$$

The two following relations are evident.

$$(37) \quad \Delta_2 \theta = \left(\frac{\partial \theta}{\partial v} \right)_q \Delta v.$$

$$(38) \quad \Delta_1 \theta = \left(\frac{\partial \theta}{\partial v} \right)_p \Delta v.$$

There follows at once

$$(39) \quad \frac{C_p - C_v}{C_v} \left(\frac{\partial \theta}{\partial v} \right)_p = - \left(\frac{\partial \theta}{\partial v} \right)_q,$$

or

$$(40) \quad \gamma = 1 - \left(\frac{\partial v}{\partial \theta} \right)_p \left(\frac{\partial \theta}{\partial v} \right)_q.$$

By a process very similar to that involved in (8), (9) and (10), we get

$$(41) \quad \left(\frac{\partial \theta}{\partial v} \right)_q = \left(\frac{\partial \theta}{\partial v} \right)_p + \left(\frac{\partial \theta}{\partial p} \right)_v \left(\frac{\partial p}{\partial v} \right)_q.$$

The application of (8) to an isopiestic process gives

$$(42) \quad \left(\frac{\partial v}{\partial \theta} \right)_p \left(\frac{\partial \theta}{\partial p} \right)_v = - \left(\frac{\partial v}{\partial p} \right)_\theta.$$

Equations (40), (41) and (42) give at once

$$(43) \quad \gamma = \left(\frac{\partial p}{\partial v} \right)_q \left(\frac{\partial v}{\partial p} \right)_r,$$

which is the equation expressing Reech's theorem. In case (43) is applied to finite changes in which the changes in specific volume are small and equal, we have as a first approximation

$$(44) \quad \gamma = \frac{\Delta p_q}{\Delta p_r}.$$

This is the form which has been used in the present work.

It was originally planned, and the apparatus was constructed with the aim in view of measuring both Δp_q and Δp_r directly with the apparatus. This general method was attempted, though no satisfactory results were obtained thereby. After repeated failures to get consistent values of γ , the plan was modified. According to this method Δp_q was measured as planned; Δp_r , however, was computed. The methods of obtaining Δp_q and Δp_r will be considered later.

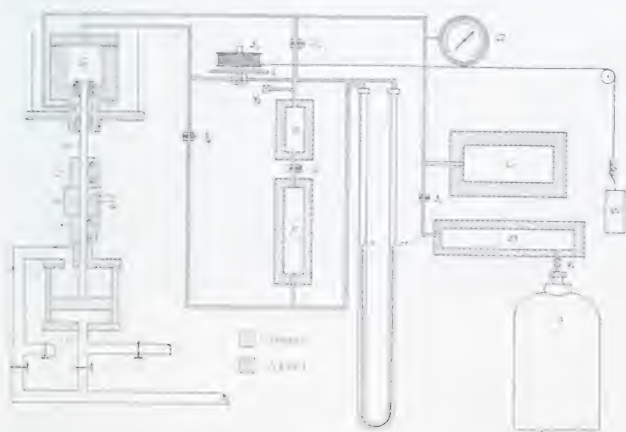
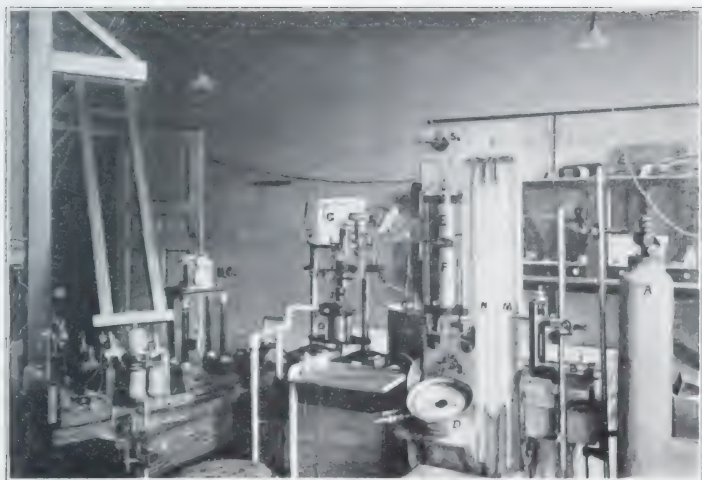


Fig. 5.

Apparatus.—The apparatus and the method of experimentation may be seen from an inspection of Fig. 5 (see also Plate I.) which represents the essential portions of the apparatus as finally connected and used. In general the arrangements and the materials have been so chosen as to withstand with safety pressures of 100 atmospheres though the actual

highest pressure attained in these experiments was about 57 atmospheres. *A* represents the tube containing CO_2 under pressure which in the experiments to be considered was the source of the gas and of the pressure. *B* represents a cylinder of about 250 cm.³ capacity containing phosphorous pentoxide sprinkled through cotton-wool for the purpose of removing the moisture from the gas passing through it. *C* represents a distributing chamber of about 600 cm.³ capacity which also served as a maintainer of the pressure in the protective system to be spoken of later. At the stop-cock *S*₂, the gas enters the system where it is to be experimented with. *D* is a Bourdon steam test-gauge reading to 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ by steps of $5 \frac{\text{lbs. wt.}}{\text{in.}^2}$. *E* and *F* are chambers of respectively 150 cm.³ and 300 cm.³ capacity connected with the arms *M* and *N* of the differential, mercurial manometer. This manometer also served as a manoscope. The combination is the same as that used by Maneuvrier in his original work. The purposes of *E* and *F* are merely to give large volumes to the gas chambers of the manometer so that, in case a small leak should occur in either of these gas chambers, the rate of change of pressure in it should be negligible. *E* and *F* are separated by a stop-cock *S*₅ which in the final arrangement was not used. *G* is the compression chamber which contains the gas to be compressed or rarified. It has a capacity of about 300 cm.³ and is surrounded by a bath which contains a thermoregulator and a stirrer (not shown in Fig. 5 nor in Plate I.). The volume of *G* can be increased or diminished at will by means of the device indicated at *O* which is actuated by compressed air. Chambers *B*, *C*, *E*, *F* and *G* are all japanned on the inner surfaces for the purpose of preservation and chamber *G* for the added purpose of surrounding the contained gas with a poor conductor for heat. *H* is a piston rod to which are clamped two stops *I* and *J* which are separated by a block of hard oak wood *K*. The use of different blocks of wood for *K* permits of different changes of volume in chamber *G* due to the thrusting in of the piston rod *H*. The lower stop *J* is firmly fixed to the rod *H* in order that, when *H* is in its lowest position, the volume of *G* is certain to be very closely a fixed amount. *V*₁ and *V*₂ are pin valves. *S*₁, *S*₂, *S*₃, *S*₄ and *S*₅ are stop-cocks. As already noted, *S*₅ was not made use of in the apparatus as finally arranged. The construction of *S*₃ is shown in Fig. 6. *S*₁, *S*₂, *S*₄ and *S*₅ differ from *S*₃ only in having the special device attached to the pin of *S*₃ replaced by a bar so that the pin may be rotated by hand. The pin of *S*₃ is rotated by a heavy weight *W* attached to a heavy spring which in turn is attached to a slender rope made of several strands of heavy fish-line, one end of which is wound about the wooden drum fastened to the pin of *S*₃. The pin of *S*₃ is provided with an arm *L* which serves



A. G. WORTHING.

PLATE I.

as a catch. The spring removes the sudden jolt that otherwise would be experienced on the sudden stoppage of the rotation of the pin of S_3 . The final ground surfaces of the pin and stock were produced by grinding them in powdered quartz and, sometimes, in pumice. In Fig. 5 a small tube is shown connecting C with P . The pressure in C was always nearly equal to that in the system $EFGMN$. Consequently this connection at P together with the packing about H permits at the most, of only a slow leakage of gas into or out of G through the packing and along the surface of H . Similar tubes lead from C to all the stop-cocks. They are connected to the stop-cocks at points which lead directly to the grooves Q (Fig. 6). These grooves entirely surround the pin of the stop-cock. As before the pressure in C is distributed through the tube to Q where it

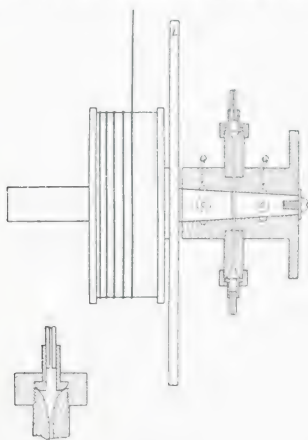


Fig. 6.

prevents the leakage of gas from or into the system $EFGMN$. The small tubing connecting the various chambers and stop-cocks is of copper. The external and internal diameters are respectively .32 cm. and .16 cm. The method of making the unions of these tubes with the other portions of the apparatus is well illustrated in Fig. 6. The external and internal diameters of the glass tubing used in the manometer are respectively .80 cm. and .30 cm. The stop-cocks are of brass, the chambers B , C , E , F and G were cut out of steel shafting.

In the method of experimentation pursued it was necessary to vary and to measure the time interval between the compression of the gas in G (Fig. 5) and the opening of the S_3 . This was brought about by means of the apparatus diagrammed in Fig. 7. The block of oak wood,

K (Fig. 5) carries a projecting metal prong *a*. The thrusting in or out of *H* brings *a* in contact with *b* and *c*. The contact *ab* closes an electrical circuit through the electro-magnet *d*, the energizing of which releases a pendulum which in its motion closes at *e* an electrical circuit through the electro-magnet *f*, opens at *g* the same circuit, and breaks at *h* by a device not indicated, the circuit containing the electro-magnet *d*. The current through the circuit closed at *e* actuates the electromagnet *f*, thus releasing the catch *L* attached to the pin of stop-cock *S*₃. The weight *W* causes the rotation of the pin of *S*₃. The breaking of the

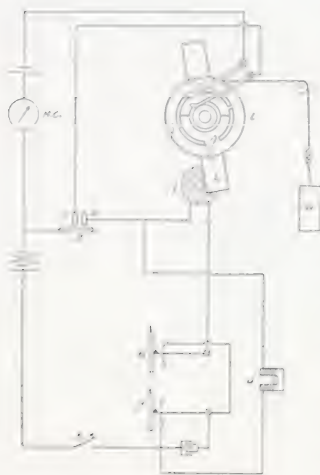


Fig. 7.

circuit at *g* is followed by the demagnetizing of *f*, and the catch *L*, after a rotation of the pin of 180°, is caught and the rotation of the pin is suddenly stopped. In case there is contact at *e* when the plunger *H* is moved in, the electromagnets in the circuits at *d* and *f* are actuated simultaneously. Thus by having the circuit at *e* initially closed or broken two different time intervals may be had between the compression of the gas in *G* and the opening of the cock *S*₃. Other intervals may be had by varying *W* and the position of *e* on the pendulum apparatus. The contact *ac* permits a current to flow through the commutation device on the drum *i* of *S*₃ through the electro-magnet of a Hipp's chronoscope

(H.C.). At *j* this current is broken when the stop-cock *S*₃ is open, as may be seen by inspecting the diagram of the commutating device. *S*₃ is diagrammed in a closed position. Thus the chronoscope records the time elapsing between the plunging in or out of *H* (Fig. 5) and the opening of the stop-cock *S*₃. Previous to July 28th, however, a slightly different method was used. The interval measured was from the plunging in or out of *H* to the closing of *S*₃.

Stop-cock Difficulties.—Originally it was planned to use tallow as the stop-cock lubricant, and to have the openings to *Q* and the grooves *Q* of the stop-cocks (Fig. 6) filled with gas directly connected with that in *C*. It was soon very evident that this plan must be abandoned. With this arrangement, pressures of a few atmospheres could be maintained for an hour at most. A great deal of time was spent in the search for some

stop-cock fluid which should be able to withstand the high pressures. The fluid finally used was formed by dissolving approximately one part of rubber in three parts of hot pine-tar. The solution was heated and the more volatile gases driven off until the desired consistency was reached. This fluid when cool is very viscous and sticky. It was introduced in the openings leading to *Q* and in the grooves *Q*. It did quite well and often for several hours, no noticeable leaks in the apparatus could be detected. With the very highest pressures the fluid was gradually forced out between the pin and the stock of the stop-cocks. However, there was no leakage of gas to the outside, until a complete passage-way to the outside for the gas back of the rubber-tar solution had been formed. As soon as such a passage-way was formed, the desired gas pressure in *C* was usually very hard to maintain by the admission of gas through *S*₁ and it was necessary to discontinue the experiment, empty the apparatus and refill the receptacles with the rubber-tar solution. For further work with this apparatus, considerably enlarged receptacles for the stop-cock fluid should be provided.

The Experimental Determination of Δp_0 .—In the filling of the apparatus with the gas to be experimented upon, it was necessary to be sure that the gas was dry and that whatever air was in the apparatus initially was removed or nearly so. The moisture was removed by the phosphorus pentoxide in *B* (Fig. 5). The phosphorus pentoxide was replaced by a fresh supply several times. In each instance, that furthest from the entrance to chamber *B* was found when removed to be a dry powder, thus indicating that in all cases the carbon dioxide gas experimented on was free from moisture. The removal of the air was accomplished partially with a hand pump, then carbon dioxide was allowed to fill the exhausted space. This mixture of air and carbon dioxide was then pumped out and the process repeated until it was certain that not more than .05 per cent. of the gas in the apparatus was of the original air. After the desired pressure throughout the apparatus including the protective system had been reached and had become steady due to the temperature having reached a steady state, *S*₃ was closed. Then, depending on whether the change in the compression chamber *G* was to be a compression or a rarefaction, the pressure in the protective system and in *E* and *M* was increased or decreased until the expected change in pressure in the compression chamber was equal to the difference indicated by the mercury levels in *M* and *N*. Then *S*₄ was closed. At this stage, it is to be kept in mind, the pressure in the compression chamber *G* was the same as that in *F* and that at the upper surface of the mercury in *N*; and that the pressure in *E* was the same as that in *M*. Now with the rapid successive opening and closing of the valves letting compressed

air into and out from O , the gas in G was compressed or rarified due to the motion of the piston H . contact was made at ab and ac (Fig. 7), as explained above; the pin of S_1 was rotated connecting for a short space of time chambers E and G ; and the time interval between the making of the contact ac and the opening of S_1 was recorded by the Hipp's chronoscope H.C. This was very quickly followed by the reverse movement of the piston H in order that there might be but a very small amount of heat lost or gained by the gas in the compression chamber as a result of the heating or cooling from the previous direct motion of H . In case the pressures in G and M were not equal on the opening of S_3 , a passage of gas must necessarily have taken place through S_3 ; and, on the return of H to its initial position, S_4 was opened. There was a readjustment of pressure then in G , F , and N and also in E and M . When a steady state was reached, usually after a minute or so, the process beginning with the closing of S_1 was repeated. In fact it was necessary to repeat again and again until, by the automatic transference of gas through S_3 from G into E or vice versa, there should occur for at least for two successive repetitions no transference of gas from E to G or vice versa. This condition was determined by an observer looking through a cathetometer telescope at the upper mercury surface in M or in N . Whenever in the process described above there occurred a transfer of gas from G to E or vice versa, there was a shift in the mercury level. When a condition of balance obtained, no further shifting of the mercury surface could be noted, in fact no distortion of the surface could be detected. With the apparatus in working order, it usually did not require more than ten trials before the balance was obtained. The actual difference of pressure produced in the compression chamber and existing after the time interval shown by the Hipp's chronoscope, was measured on the differential manometer MN by means of the cathetometer. By varying the initial conditions at the contact e (Fig. 7), data corresponding to two time intervals may be obtained.

Now, if it may be assumed here that the change in the *change in pressure* due to heat being conducted to or from the gas in G is a linear function of the time for short intervals of time, we may obtain the change in pressure which would have occurred in G if the time interval had been infinitesimal. Let Δp_1 and Δp_2 be changes in pressure and Δt_1 and Δt_2 be the corresponding intervals of time in the above described experiment. Let Δp_0 be the change in pressure for an infinitesimal interval. Then we have

$$(45) \quad \Delta p_0 = \Delta p_1 - \frac{\Delta p_2 - \Delta p_1}{\Delta t_2 - \Delta t_1} \Delta t_1.$$

Δp_0 is the Δp_q of (44). Data from certain preliminary measurements obtained July 25 and platted in Fig. 8, indicate that the assumption is not far from true. Near the completion of the experimental work, other attempts were made to test (45) more carefully. In each instance, certain accidental changes occurred which made impossible the obtaining of the desired number of different intervals under conditions which would be necessary for a rigid test. Even if the assumption made is not true, the actual variation from it could hardly be such as to cause any serious error.

It is perhaps well to note here certain precautions taken to insure accuracy. The pressure gauge was always adjusted so that the index was aligned with some desired division on the dial. The face of the gauge was always tapped lightly to insure the freedom of movement of the indicating parts. Parallax was

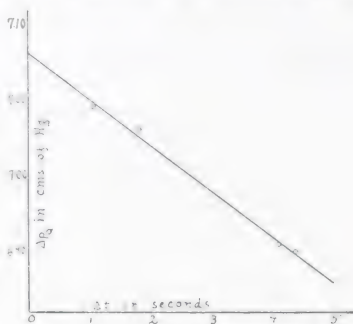


FIG. 8.

Experimental test of assumption made in (45)

carefully eliminated. A single division on the dial corresponded to 5 lbs. wt. in.². A variation of one twentieth

of a division was noticeable. This corresponds to about one sixtieth of an atmosphere. Actual trials showed that any desired pressure could be certainly obtained (assuming the gauge to be correct) to within 1.5 cm. of Hg. To prevent any errors due to the sticking of the mercury in the manometer tube, the glass tubes *M* and *N* were tapped just before and just after the compression or rarefaction in *G* was produced. To further eliminate such troubles, the initial pressure in *E* for one determination of Δp_q for a given *p* and *T* was first made too great and for the next determination under the same conditions was made too small, in order that in the self-adjusting process there would in the first case be a slight movement of the mercury in *N* upwards and then in the second case downwards. The two values of Δp_q obtained thus were always in very good agreement, they always differed in such a manner as to indicate that there was some sticking of the mercury to the manometer tubes. These differences in Δp_q , with a few exceptions relating to measurements especially difficult, did not amount to more than .6 mm. of Hg and usually were much less. The average of two such values for Δp_q were taken as

the observed value. When it is considered that the actual values of Δp_Q varied from 5 to 13 cm. of Hg, it will be seen that the uncertainties arising from this source will generally be quite small. In order to eliminate any errors in the measurement of Δp_Q due to leakage of gas during the measurements of the heights of the mercury columns in M and N , one observer noted during this process with the aid of a traveling microscope the slow motion, if it existed, of the mercury in column M . Corrections to the cathetometer readings for such leakages were readily made. In addition to the ordinary precautions for cathetometer work, double settings were made. If the readings from these double settings were not consistent with the difference noted on the traveling micrometer, further readings were taken.

In order that a clear idea of the method of procedure may be obtained, certain of the records for the afternoon of August 12 are presented in Table VIII., together with certain explanatory notes. C and R indicate

TABLE VIII.

Sample note book records showing experimental details for determination of Δp_Q .

Aug. 12, 1910, P. M.

Movement of compressing piston with blocks no. 3 and no. 4 at K (Fig. 4).

Mean of five determinations at the beginning 1.435 cm.

Mean of five determinations at the end 1.426 "

Av. 1.430 "

Gauge reading: $300 \frac{\text{lbs. wt.}}{\text{in.}^2}$.

Collected data:

Room Temp.	Bath Temp.	Change	N in cm.	V in cm.	$M-N$ in cm.	Adjustment.	Interval in Sec.	Remarks.
26.6°	30.0°	C	92.672	83.395	9.277	down	.095	?
.6	"	"	.658	.412	.246	up	.098	good
.6	"	"	.627	.430	.197	down	.070	good
.2	"	"	.610	.470	.140	down	.314	
.4	"	"	.630	.435	.195	up	.310	
.4	"	R	82.321	92.552	.231	up	.090	
.2	"	"	.340	.540	.200	down	.090	
.2	"	"	.365	.516	.151	up	.304	
.1	"	"	.390	.515	.125	down	.304	

Note book records from which N , M and interval entries of the fourth observation were taken:

N in cm.	Microscope Reading.	Cathetometer Interval.	N in cm.	M in cm.	$M-N$ in cm.	Traveling Microscope Reading in cm.
32.61	005			92.610		8.911
	153	158	32.60	.605		15
.60	322	150	.59		83.480	19
.59	475	153	.59		.480	21
.59	632	157	.59	Corrected 92.610	83.470	

respectively a compression and a rarefaction. The N and M readings are the cathetometer readings on the mercury menisci in tubes N and M (Fig. 5). $M \sim N$ represents the numerical difference between M and N . The adjustments "up" and "down" indicate that, in the self-adjustment of the gas pressure preceding the equilibrium, the motions of the mercury surface in N during a compression and in M during a rarefaction were "up" and "down" respectively. The "interval" measured is the time elapsing between the making of the circuit at ac (Fig. 7) and the breaking of the circuit at j . It is thus the interval between the plunging in of the piston H and the opening of stop-cock S_3 so that chambers E and G were in communication. Under remarks it is noted that the first observation was considered questionable when taken. It does not check up with the other observations from the standpoint of the variation in Δp_g due to up and down adjustments. It has been discarded in the further computational work. The readings N' were read on a rough paper scale back of tube N with the aid of the cathetometer telescope, just before the gas in G was compressed; the readings N'' were taken in a similar manner just after. The unit of the chronoscope readings was .002 sec. The average interval was therefore .314 sec. The slight variations in the individual intervals are partially to be accounted for by the fact that the weight W (Fig. 5) was usually still being vibrated up and down somewhat by the spring above it when a new compression was about to be made. The method of obtaining the corrected N and M readings is evident. From the collected observations given, there are to be obtained as indicated above with the aid of (45) and on correcting $M \sim N$ to 0°C. , data recorded in the first six columns of Table XIII. under the proper date. Nearly all such data relating to Δp_g represent values obtained in the manner indicated above, with the exception that usually only two observations, one an "up," the other a "down" for the same interval were taken either for the rarefaction or for the compression. In computing Δp_g by (45), the term multiplying Δt_i was assumed to be the same as in the other process for which the regular four observations were taken.

The Computations for Δp_a .—Kamerlingh Onnes²¹ has given an empirical equation of state for CO_2 which is founded on Amagat's work and which represents Amagat's data with a very high degree of accuracy. The equation is of the form

$$(46) \quad \lambda p v = A + \frac{B}{\lambda v} + \frac{C}{(\lambda v)^2} + \frac{D}{(\lambda v)^3} + \frac{E}{(\lambda v)^6} + \frac{F}{(\lambda v)^8},$$

where

$$(47) \quad \lambda = \frac{\hat{p}_c \hat{v}_c}{\theta_c}, \quad p_c = \frac{p}{\pi}, \quad \theta_c = \frac{\theta}{\tau} \text{ and } v_c = \frac{v}{v},$$

In the computations connected with the present work the values of v were expressed for the most part in $\frac{\text{N. V. units}}{\text{gr. mol.}}$ in order to check the computations based on K. Onnes's equation with the experimental data of Amagat.²⁹ In determining Δp_θ the following expansion was used

TABLE X.

Values of β for equation (50).

P in Atmos	7.78	14.72	21.52	28.52	35.52	42.34	49.35	57.0
0° C.	.94	.88	.78	.66				
30	.96	.92	.87	.81	.74	.66	.55	.39
50	.97	.94	.90	.86	.82	.77	.71	.63
100	.98	.96	.95	.93	.91	.89	.87	.84

hundredth. Column 7, Table XI. contains the results of such computations for Δp_θ .

Calibrations and Miscellaneous Notes.—It should be noted here that various parts of the apparatus were carefully calibrated and measured. The differential surface tension effects in the manometer were always negligible. The changes in the density of the mercury due to the varying pressure were also found negligible. It was always to be noted on releasing the pressure in the apparatus that some CO_2 had been dissolved in the mercury. The amount was small, and, considering the limited amount of time at the writers' disposal, it never seemed sufficient to warrant an investigation. The possible effect of the dissolved CO_2 on the density of the mercury has been ignored. The pressure gauge was a Bowden steam test gauge of 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ range. It was carefully calibrated. In determining the pressure of the gas in the apparatus account was taken of the barometric pressure. Throughout the time of experimentation this was .97 atmo. The thermometers were compared with standard thermometers. The volume of the compression chamber was obtained by finding the weight of the water necessary to fill it. The

TABLE XI.

Data for and results on γ for CO_2 . Preliminary Results.

Date.	Temp. of Bath.	β in Atmos.	Change.	Piston Motion in cm.	Δp_θ in cm. of Hg .	Δp_θ in cm. of H_2O .	γ	γ (corr.)	γ	Purity of CO_2 in %.
July 22	29.4	14.72	C	3.004	13.10	9.77	1.342	1.340		99.2
25	32.7	7.78	C	3.004	7.04	5.37	1.310	1.311		99.6
27	32.4	14.72	C	3.004	13.24	9.79	1.352	1.350		
30	32.2	28.52	C	1.422	12.09	8.04	1.503	1.508		
Aug. 1	31.0	7.78	C	1.422	3.348	2.529	1.324	1.325		
3	31.4	7.78	C	1.422	3.337	2.528	1.320	1.320		
4	31.8	7.78	R	1.422	3.326	2.507	1.326	1.327		
5	31.7	7.78	C	2.122	4.94	3.48	1.306	1.306		
5	31.4	7.78	C	2.122	4.97	3.78	1.314	1.315		

TABLE XI.—Continued.

Data and results on γ for CO₂. Final Results.

Date.	Temp. Bath	Pressure Atmos.	Change	Piston Motion in cm.	Δp in cm. of H ₂ O	Δp in cm. of H ₂	γ	γ (corr.)	γ'	Purity of CO ₂ in %.
8	31.3	7.78	C	3.004	7.09	5.37	1.320	1.320	1.268	
9	30.8	7.78	R	3.004	7.01	5.32	1.317	1.317	69	
	31.5	14.72	R		13.20	9.71	1.359	1.360	63	
	32.2	14.72	R	1.422	6.18	4.60	1.344	1.346	50	
	31.7	14.72	C	1.422	6.23	4.61	1.352	1.353	51	99.6
10	31.2	28.52	C	1.428	12.05	8.09	1.488	1.489	50	
	31.8	28.52	R	1.428	12.14	8.06	1.505	1.509	63	
11	31.3	21.52	R	1.407	9.06	6.32	1.432	1.433	63	99.6
	31.2	21.52	C	1.407	9.09	6.34	1.434	1.434	62	
12	49.8	7.78	C	2.994	6.99	5.39	1.296	1.296	54	
	49.9	7.78	R	2.994	7.04	5.34	1.316	1.316	51	
	49.9	14.72	R	2.994	13.11	9.91	1.335	1.335	60	
	49.9	14.72	C	2.994	13.29	9.89	1.345	1.345	62	
13	50.0	21.52	C	1.430	9.19	6.63	1.386	1.386	57	
	50.0	21.52	R	1.430	9.20	6.61	1.391	1.391	65	
	50.0	28.52	C	1.421	12.15	8.39	1.448	1.448	61	
	50.1	28.52	R	1.421	12.10	8.37	1.447	1.447	64	
15	50.2	34.52	R	.768	8.20	5.38	1.524	1.525	69	
	50.2	34.52	C	.768	8.16	5.39	1.515	1.516	62	
	98.4	7.78	C	3.020	6.93	5.52	1.256	1.256	35	
	98.4	7.78	R	3.020	6.91	5.47	1.264	1.264	47	
16	98.5	14.72	C	1.436	6.17	4.86	1.269	1.269	27	
	98.4	14.72	R	1.436	6.17	4.84	1.275	1.275	34	99.5
	98.5	28.52	C	1.438	12.06	9.07	1.329	1.329	36	
	98.5	28.52	R	1.438	11.99	9.04	1.326	1.326	36	
17	98.6	41.34	R	1.775	9.83	6.96	1.412	1.413	66	
	98.6	41.34	C	1.775	9.77	6.97	1.401	1.402	55	99.3
	0.2	28.52	C	.786	6.49	3.83	1.694	1.694	48	
	0.2	28.52	C	1.425	11.91	6.95	1.710	1.710	34	
18	0.2	28.52	R	1.425	11.81	6.94	1.702	1.702	32	
	0.2	21.52	C	1.424	8.97	5.07	1.528	1.528	32	
22	30.9	41.34	C	.786	9.93	5.61	1.771	1.770	59	
	0.2	7.78	C	2.120	4.95	3.70	1.338	1.338	58	
23	0.2	7.78	R	2.120	4.95	3.67	1.346	1.346	68	
	98.6	34.52	C	.805	8.24	6.19	1.331	1.332	14	
24	98.6	34.52	R	.805	8.27	6.18	1.339	1.340	24	
	98.6	48.36	C	.809	11.78	8.28	1.423	1.425	50	
25	31.6	7.78	C	4.388	10.31	7.88	1.309	1.309	57	
25	30.7	57.0	C	.798	13.78	5.85	2.36	2.35	82	
	31.1	7.78	C	3.038	7.12	5.43	1.310	1.310	58	

γ (corr.) indicates values of γ corrected to the standard temperatures 0°, 31°, 50° and 98.5° C.

volume of the chamber and its accessories is 310.0 cm³. The average of 20 measurements of the diameter of the compressing piston gave 1.1098 cm. The purity of the gas was determined by bringing a known quantity of it into contact with KOH.

The time required for the thrusting in of the plunger *II* (Fig. 5) is a matter of some interest. If the thrusting in of the plunger and the reaching of a steady state by the gas could possibly occur in an extremely short interval such as .001 sec., one would need to give special consideration to the extremely high temperature gradient which would be established at the boundaries of the vessel. If, however, each of the two processes should take an appreciable time, no very high temperature gradient is to be expected at any instant. The time of intrust of the plunger *II* was determined by taking the difference between two selected intervals. The first interval was from the starting of the plunger *II* to the opening of stop-cock *S*₂, the interval being recorded in the manner described above by the chronoscope. The second interval differed from the first in that the contact beginning the interval was made near the end of the intrust instead of at the beginning. The average of several such determinations showed that the time for the maximum intrust was about .06 sec. In the measurements made this interval of intrust was always included. Of course, for the smaller intrusts, this interval was smaller.

Data and Results.—The data taken and the values of γ obtained are shown in Table XI. The values given may in a few cases differ by .001 from the quotient of Δp_g by Δp_s because of the manner in which the former were obtained. The corrections for obtaining γ (corr.) for the four standard temperatures were obtained from an initial rough plot. The computed values of γ for these four standard temperatures have been plotted in Fig. 9 as a function of the pressure. With a few exceptions, each plotted point represents the mean of two determinations of γ , one from a compression, the other from a rarefaction. Two pairs of such values have been included in the point for the gas at 31° C. and a pressure of 7.78 atmospheres. The higher values were obtained early in the work. The lower values were obtained near the end. Sometime between August 18 and August 23, the date unfortunately not being recorded, the rubber washer between the compression chamber and its lid was replaced by a new one, which was noticeably thicker than the one removed. The importance of the consequent change in the volume of the compression chamber was not appreciated fully at the time or accurate measurements would have been taken. Account has not been taken of this change in the computations. However, if account should be taken of this change of volume, the separately determined values would more nearly coincide. The same is to be said regarding the values for γ at 98.5° C. for pressures of 35.52 atmospheres and 49.36 atmospheres. In this instance the values of γ taking account of the volume change

would also be raised so that the variations of the plotted γ for this temperature would be less noticeable. The same possibility applies to γ for 11.2° C. at 7.78 atmospheres. It is to be noted that the preliminary values of γ , though not plotted, agree very well with the final results.

Result of Maneuvrier and Results Based on C_v by Joly.—There is plotted for comparison purposes the value of 1.298 determined by Maneuvrier,³⁷ the originator of this method, for CO₂ at atmospheric pressure and 10° C. Values of γ for CO₂ at atmospheric pressure have been rather discordant. Generally, however, such values approximate the results obtained here,

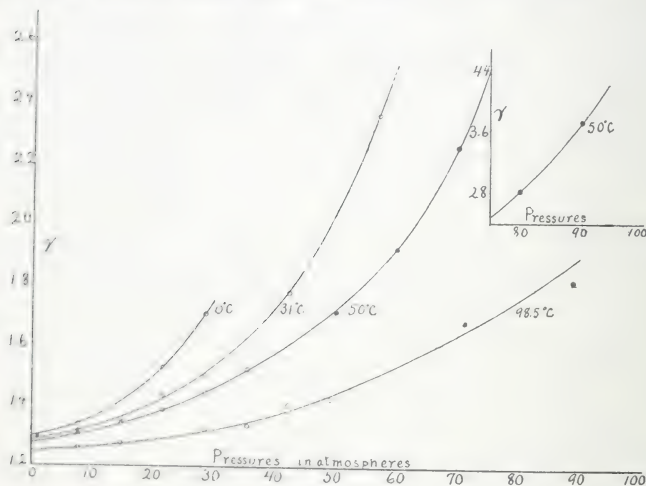


Fig. 9.

Variation of γ in CO₂ with pressure and temperature.

Results based on determinations

of C_v by Joly		●
of Δp_v by Worthing		○
of Maneuvrier		+

though the variation with temperature has been found to be less noticeable than what the writer has obtained. There are also plotted values of γ which are based on determinations of C_v by Joly. The method of computing was that used by Amagat.³¹ Values of C_v and p, v, θ relations from the experimental data of Amagat were combined according to (13). This has been done by Amagat. The writer has not been able to verify fully the computations of Amagat and has here incorporated results from his own computations. The writer in determining $(\partial p'/\partial \theta)_v$ and $(\partial v/\partial \theta)_p$

has used a graphical method. The values determined represent true values for the temperatures and pressures indicated. The values of C_v for pressures of 80 and 90 atmospheres at 50° C. have been taken from Amagat's extrapolation. The values for C_v at 100° C. result directly from equations given by Joly for CO_2 at densities .1240 gr. cm.³ and .1800 gr. cm.³ Table XII. includes these data and results. The general agreement is quite satisfying.

TABLE XII.

Data for and results on γ for CO_2 based on C_v determinations by Joly and p, v, θ determinations by Amagat.

T	p	C_v	$C_v \left(\frac{\partial v}{\partial \theta} \right)_p$	$-\left(\frac{\partial C_v}{\partial v} \right)_p$	C_p	γ
50°C.	50	.1920	.081310	2020	.329	1.710
	60	.2015	1280	2850	.386	1.915
	70	.2108	1345	3670	.474	2.245
	80	.2303	1530	4560	.644	2.83
	90	.2585	1800	5500	.945	3.73
100	71.3	.1902	0870	3690	.318	1.670
	87.8	.2056	0805	5590	.372	1.810

p is expressed in atmospheres, C_p and C_v in cal. and v in N. V. units
gr. $\times$ deg. gr. mol.

γ' of Equation $pv^{\gamma'} = \text{constant}$.—In the column (Table XI.) headed γ' are included values which are derived on the assumption that for the processes of compression and rarefaction considered, there holds the following relation:

$$(52) \quad pv^{\gamma'} = \text{constant}.$$

The approximate constancy of γ' for a given temperature is remarkable and is worthy of further experimental consideration. A γ' , of course, is not to be interpreted as a ratio of the two heat capacities except perhaps for the gas under zero pressure at the same temperature, or as described by the same adiabat, or under some other similar conditions. Differentiation of (52) and the application of (43) give

$$(53) \quad \left(\frac{\partial p}{\partial v} \right)_\theta = -\gamma' \frac{p}{v} = \gamma \left(\frac{\partial p}{\partial v} \right)_\theta.$$

Whence

$$(54) \quad \gamma = -\gamma' \frac{p}{v} \left(\frac{\partial v}{\partial p} \right)_\theta,$$

or according to Bakker³⁰

$$(55) \quad \frac{\gamma - \gamma'}{\gamma'} = -\frac{p}{v} \left(\frac{\partial v}{\partial p} \right)_\theta - 1 = \text{departure of gas from Boyle's law.}$$

Extrapolation to zero pressure, making use of these values of γ' , would seem to indicate that the plotted curves of γ (Fig. 9), on being extrapolated back to zero pressure, had been extrapolated to too high values of γ . Not a great deal of dependence may be placed on this, however, until more is known about the function γ' .

Conclusions regarding γ and γ' .—The plats and tables show for CO_2 for the region considered:

1. The ratio of the two heat capacities γ for a given pressure decreases with an increase of temperature.
2. γ for a given temperature increases with pressure.
3. The curve for γ at 30°C . is such as to be consistent with the theoretical infinite value of γ at the critical point.
4. The agreement of the values based on Δp_v data with those based on C_v data by Joly is very good.
5. The results at atmospheric pressure are in fair agreement with the results of others.
6. γ' , where $p v^{\gamma'} = \text{constant}$ applies to reversible adiabatic changes, is approximately constant.

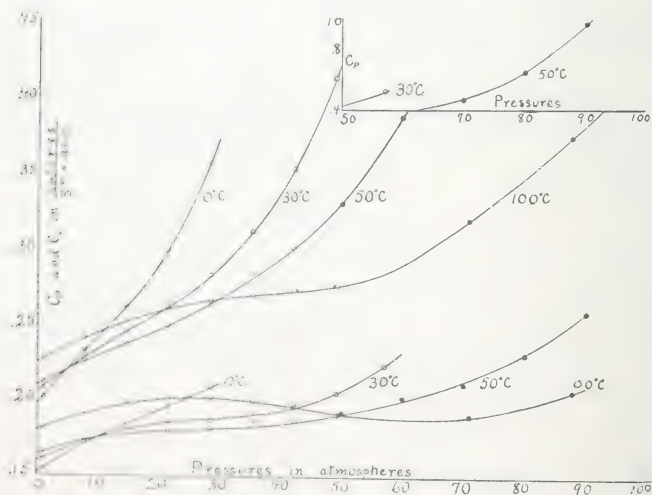


Fig. 10.

Variation of C_p and C_v of CO_2 with pressure and temperature.

Results based on determinations

of C_v by Joly. ●

of γ by Worthing. ○

V. DETERMINATION OF C_v AND C_p FOR CO_2 .

Determinations from the Present Work.—Equation (13) gives at once

$$(56) \quad (\gamma - 1)C_v = v \left(\frac{\partial p}{\partial \theta} \right)_v \left(\frac{\partial v}{\partial \theta} \right)_p.$$

This enables one to determine C_v and hence C_p by means of the data already obtained. The method of computation is evident. The transformation factor used in this work in the changing of the units of C_v and C_p to the ordinary units is expressed in (57).

$$(57) \quad 1 \frac{\text{atmos.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}} = 12.24 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$$

Values of C_v and C_p are to be found in Table XIII. Values of $(\partial p / \partial \theta)_v$, $(\partial v / \partial \theta)_p$ and $\theta(\partial p / \partial \theta)_v(\partial v / \partial \theta)_p$ are included in the hope that they may save some one otherwise extended computations. In Fig. 10 C_v and

TABLE XIII.

Data for and results on C_p and C_v of CO_2 .

T	p	γ	$\log \left(\frac{\bar{v}}{\bar{c}\theta} \right)$	$\log \left(\frac{\bar{v}}{\bar{c}\theta} \right)_p$	$\log \left[v \left(\frac{\bar{v}}{\bar{c}\theta} \right)_v \left(\frac{\bar{v}}{\bar{c}\theta} \right)_p \right]$	C_v	C_p
0	7.78	1.342	.25130	.47359	.36852	.173	.233
	14.72	1.418	.8459	.5156	.8856	.184	.261
	21.52	1.528	1.0707	.4206	.9276	.196	.299
	28.52	1.702	.2630	.3796	2.0789	.209	.356
30	7.78	1.314	2.4501	.7169	3.6486	.174	.230
	14.72	1.360	.7652	.4770	.7238	.180	.245
	21.52	1.420	.9680	.3545	.8041	.186	.265
	28.52	1.509	1.1315	.2778	.8909	.187	.282
	35.52	1.621	.2727	.2362	.9905	.193	.311
	42.34	1.779	.3978	.2203	2.0997	.198	.353
	49.36	2.01	.5200	.2271	.2287	.205	.412
	57.0	2.37	.6540	.2602	.3958	.223	.528
50	7.78	1.304	2.4143	.7092	3.6328	.173	.226
	14.72	1.340	.7208	.4620	.6921	.177	.237
	21.52	1.386	.9159	.3291	.7543	.180	.249
	28.52	1.447	3.0709	.2414	.8216	.182	.263
	35.52	1.521	.1997	.1826	.8916	.187	.284
	42.34	1.603	.3100	.1441	.7964	.187	.300
100	7.78	1.260	2.3401	.6966	.6085	.191	.241
	14.72	1.272	.6359	.4376	.6453	.199	.253
	21.52	1.291	.8188	.2920	.6826	.202	.261
	28.52	1.319	.9602	.1887	.7207	.202	.266
	35.52	1.353	1.0750	.1127	.7595	.199	.269
	42.34	1.392	.1699	.0551	.7968	.196	.273
	49.36	1.44	.2561	.0089	.8368	.191	.275

p is expressed in atmospheres, v in $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$ and C_v and C_p in $\frac{\text{calories}}{\text{gr.} \times \text{degree}}$.

C_p are plotted as functions of p . Values based on Joly's measurements (Table XII.) are included.

C_p Agreement with the Results of Others.—Very little agreement is to be found between the values of C_p here computed and the values of C_p obtained from a plot of Lussana's⁴³ results. The values of C_p for a pressure of one atmosphere as determined by the direct experiments of Holborn and Austin⁴² and by those of Swann⁴³ and as computed here are included in Table XIV. Excepting for the 100° C. value, the com-

TABLE XIV.
Values of C_p for CO₂ at atmospheric pressure expressed in $\frac{\text{cal.}}{\text{gr. } \Delta \text{ deg.}}$.

t	Holborn & Austin	Swann.	Worthing.
0	.203		.202
20		.202	
30	.207		.208
50	.210		.212
100	.216	.221	.228

puted results agree very well with the results of Holborn and Austin. At 100° C. the agreement is not good, though a better agreement is to be found with Swann's value for this temperature.

Causes for Possible Experimental Error.—Realizing early that the values for γ at 100° C. were slightly lower than was expected, special care was taken with the measurements. It is also, of course, an open question whether or not Kammerlingh Onnes's equation, which here bridges an experimental gap from 1 to 50 atmospheres and which here reaches its upper temperature limit of application, correctly represents the interrelations of p , v and θ for this region. The writer can not see how any experimental error in his work might produce this discrepancy. The supposition that the gas in the compression chamber has not all reached the temperature of the bath would lead to a discrepancy in the opposite direction, as would also the fact that a small amount of the gas, that in a portion of the connecting tubes, is at a considerably lower temperature than the bath. The possibility of local cooling next to the plunger during a compression might be thought to explain a part of the discrepancy. But that this is of small consequence is indicated by the good agreement obtained for γ by the rarefaction and by the compression measurements (Table XI.). Moreover, any such experimental error would be effective at the higher pressures, tending to produce too high values for C_v as well as C_p , an effect which is not in evidence in comparing the present results with Joly's (Figs. 9 and 10).

C_v Comparison with Joly's Results.—The attempt to compare the results on *C_v* computed above with the direct experimental values of Joly³² has not been as thorough as might be wished due to insufficient data. Joly concluded that the variations of *C_v* with temperature were very small for densities less than .08 gr./cm.³ for the temperature interval 0° C. to 100° C. The fact that his data do not strictly bear out his conclusion was ascribed to the observational inaccuracies entering in his work at the lower densities. This conclusion was accepted in the forming of Table VI. If it is fully accepted, very little agreement is to be found between the writer's values of *C_v* and those of Joly's. Moreover, it is not compatible with the results of Holborn and Austin and of Swann on *C_p* at one atmosphere and the ordinarily accepted variations of *γ* with the temperature for the same pressure. These would require that at atmospheric pressure *C_v* should increase noticeably with temperature, a variation just the opposite of that found by Joly for the higher pressures. The writer has assumed that the apparent disappearance of a temperature effect with decreasing densities in Joly's results might have been a disappearance preparatory to a reversal of the temperature effect, and has computed from Joly's individual results what the values of *C_v* would be for certain densities and temperatures if the results were correct. In doing this Joly's equation for *C_v* at a density of .124 gr./cm.³ has been used. For the densities .0800 gr./cm.³ and .0456 gr./cm.³ values of *C_v* were obtained by the deriving of an equation holding over a portion of the temperature range in a manner similar to that used by Joly. Other values of *C_v* were obtained by a quadrature method based on the general principle that

$$(58) \quad C_v = \frac{\partial}{\partial T} \left[\bar{C}_v (100 - T) \right]_t,$$

where $\bar{C}_v$ is the mean value of *C_v* between *T* and 100° C. These results with corresponding values obtained from the writer's work are included in Table XV. The table indicates a fair agreement between the results

TABLE XV.

Corresponding values of C_v as determined by Joly and by Worthing.

<i>T</i>	<i>p</i>	$\bar{C}_v$ (Joly.)	$\bar{C}_v$ (W.)	<i>p</i>	$\bar{C}_v$ (Joly.)	$\bar{C}_v$ (W.)	<i>p</i>	$\bar{C}_v$ (Joly.)	$\bar{C}_v$ (W.)
0°	19.4	.194	.193						
30	22.6	.178	.186	36.0	.189	.193	49.0	.208	.205
50	24.6	.170	.181	40.0	.185	.186			
100	29.5	.206	.202	49.0	.200	.192			

p is expressed in atmospheres, *C_v* in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of Joly thus interpreted and the writer's. As suggested above, insufficient data may account for a part of the actual variations.

Conclusions Regarding C_v and C_p .—For the region considered in CO_2 , the following conclusions may be drawn:

1. The isometric heat capacity of CO_2 , C_v , at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.
2. For a given temperature C_v generally increases with increasing pressure. The reverse is true for a certain pressure interval at 100°C .
3. There is a good agreement between the results on C_v obtained by the writer and those obtained by Joly.
4. The isopiestic heat capacity C_p at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.
5. For a given temperature C_p increases with increasing pressure.
6. The variation of C_p at 30°C . is such as to be consistent with a theoretically infinite value at the critical point.
7. At atmospheric pressure the computed values of C_p agree well with the experimental values of Holborn and Austin and of Swann.
8. At high pressures the values found using the writer's experimental results are such as to be consistent with results based on Joly's data on C_v .
9. Very little agreement has been found between the writer's results and Lussana's results.

VI. THE FREE-EXPANSION AND JOULE-KELVIN EFFECTS IN CO_2 .

Results.—The methods of computation were those detailed in connection with the free-expansion and Joule-Kelvin effects in air. The results are to be found in Table XVI. Results for pressures of 50 atmospheres and higher for 50°C . and 100°C . have been determined by taking the results of Joly on C_v , the individual values being taken from the curves of Fig. 10. A value for both μ and η at the critical point ($p = 72.9$ atmos., $\theta = 304.5^\circ \text{K}$.) has been obtained by Keesom⁴⁴ by measuring the $dp/d\theta$ of the vapor tension curve of CO_2 at that point. Theoretically at the critical point of a substance there exists but a single value for $dp/d\theta$. This follows at once from (8), since at this point $(\partial p/\partial v)_\theta = 0$. Consequently we have

$$(59) \quad \mu_c = \eta_c = \left(\frac{d\theta}{dp} \right)_c$$

where the subscript c indicates the critical point values. These values of μ and η are included in Table XVI. The results as functions of the

TABLE XVI.

Data for and results on α and η for CO_2 . Results based on β , θ Data, equation, and on γ data by Worthing.

T in $^{\circ}\text{C}$.	β in Atmos.	$\alpha = z \left(\frac{\partial \theta}{\partial p} \right)_p$ in $^{\circ}\text{K}$.	$n \left(\frac{\partial \theta}{\partial p} \right)_p - \beta$ in Atmos.	μ in deg./atmo.	η in deg./atmo.	$\frac{\Delta \theta}{\Delta p}$
0	7.78	48.8	1.12	1.398	1.266	.144
	14.72	87.9	4.44	1.333	1.259	.302
	21.52	125.9	10.62	1.334	1.262	.494
	28.52	161.3	21.52	1.329	1.265	.750
30	7.78	38.3	.76	1.084	.979	.098
	14.72	69.5	2.93	1.051	.978	.199
	21.52	99.7	6.64	1.063	.989	.309
	28.52	128.3	12.51	1.054	.993	.440
	35.52	157.0	21.28	1.059	1.008	.600
	42.34	183.6	33.42	1.061	1.023	.790
	49.36	209.4	51.04	1.048	1.023	1.035
	57.0	235.2	79.67	.995	.985	1.40
50	7.78	33.3	.61	.926	.833	.078
	14.72	60.3	2.27	.901	.827	.154
	21.52	86.5	5.10	.905	.836	.237
	28.52	112.4	9.52	.912	.854	.334
	35.52	136.5	15.65	.914	.868	.440
	42.34	158.8	23.62	.905	.870	.560
100	7.78	24.3	.38	.618	.557	.049
	14.72	44.3	1.41	.587	.537	.096
	21.52	63.9	3.06	.586	.530	.142
	28.52	82.5	5.52	.586	.539	.194
	35.52	100.4	8.82	.591	.553	.249
	42.34	116.7	12.84	.596	.565	.304
	49.36	133.1	17.96	.604	.583	.364

Results Based on C_p Data by Joly and β , θ Data by Amagat.

50	50	183	35.6	.895	.895	.713
	60	212	58.0	.860	.850	.980
	70	240	89.8	.835	.835	1.28
	80	265	145.5	.765	.780	1.82
	90	286	230.0	.655	.670	2.62
100	71.3	190	48.4	.635	.660	.68
	87.8	221	80.2	.585	.615	.92

Results Based on β , θ at Critical Point by Keenan.

31	72.9	304	416.	.622	.622	5.71
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closely to the drawn curves. The variations here are such as would indicate that for good agreement of the results among themselves, the values of γ for the lower pressures should be somewhat less than they have been indicated to be. This is in exact conformity with the indications derived above in considering γ' of (49). However, the smallness

pressure and the temperature are platted in Fig. 11. Excepting for the values at zero pressure and at 7.78 atmospheres, the points lie very well of the terms $\theta - \tau(\partial\theta/\partial\tau)_p$ and $\theta(\partial p/\partial\theta)_\tau - p$ for low pressures might well account for the variations in μ and η in such cases.

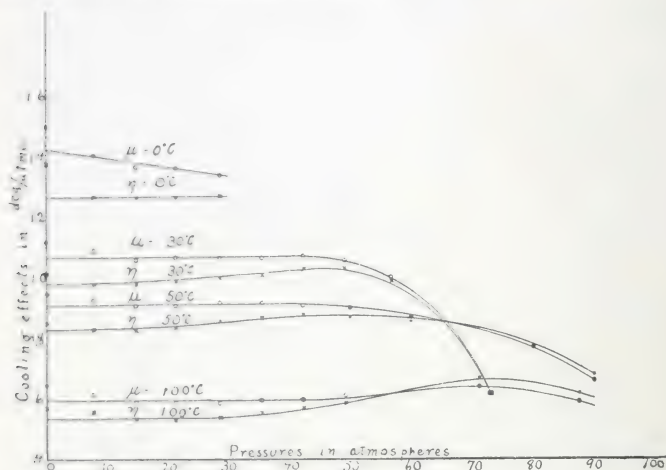


Fig. 11.

Variation of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO_2 with temperature and pressure.

Results based on determinations of

μ by Joule.....	●	■
η by Worthing.....	○	×
$\frac{dp}{d\tau}$ by Keesom.....		■

Results for Low Pressures.—In Fig. 12 there have been platted μ and η as functions of the temperature for the gas under low pressures. There have been indicated also the results of Kester,¹⁴ Joule and Kelvin,⁹ Natanson¹⁵ and some other observers. The non-agreement of μ and η at zero pressures with values at the higher pressures led the writer to consider the application of data by Chappuis¹⁶ on the p , v and θ interrelations and data on C_p by Holborn and Austin. Chappuis's results are expressed in equations of the form

$$(60) \quad pv = A + Bp$$

for five different temperatures, -17.5° , 0° , 20° , 40° and 100° C. A and B are constants. The unit of pressure used is that due to a meter

column of mercury, the unit of volume is that occupied by a gram-molecule of the gas, at 0° C., under a pressure equal to that due to a meter column of mercury. In a method exactly analogous to that used in obtaining (27) and (28), we get for $p = 0$

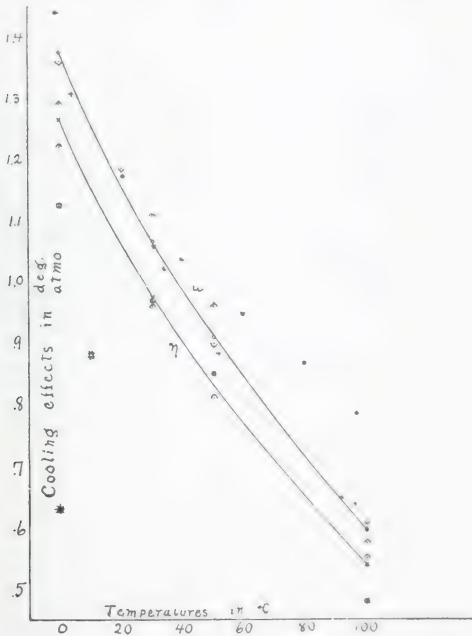


Fig. 12.

Variation with temperature of the free-expansion (η) and the Joule-Kelvin effects in CO₂ at low pressures.

Determinations of Joule-Kelvin effects

by Joule and Kelvin.....	+
by Natanson.....	∇
by Kester.....	●
from data by Chappuis and by Holborn and Austin.....	△
from Clausius's equation.....	○
by Worthing.....	○

Determinations of free-expansion effects

by Cazin.....	†
by Searle.....	*
from data by Chappuis and by Holborn and Austin.....	□
from Clausius's equation.....	○
by Worthing.....	×

$$(61) \quad \mu_0 = \frac{\theta \left(\frac{\partial B}{\partial \theta} \right)_p - B}{C_p},$$

$$(62) \quad \eta_0 = \frac{\theta \left(\frac{\partial B}{\partial \theta} \right)_p}{C_p - \frac{A_0}{\theta_0}},$$

where A_0 and θ_0 are the values of A and θ for 0° C. (61) and (62) are based on the assumption that

$$(63) \quad A = A_0 \frac{\theta}{\theta_0},$$

a condition which is necessary if the gas in question is to approach the condition of a perfect gas as the pressure approaches zero. Chappuis's constants do not quite fulfil condition (63). Slight changes were made in his values for A and B , leaving the values for A and B at 0° C. and the values of $p\theta$ at the unit of pressure unchanged, such that condition (63) was fulfilled. This seems reasonable, in view of the added fact that, of the measurements by Chappuis at three different pressures, the average pressure was about equivalent to that due to a meter column of mercury. Thus changed B is readily and with a great deal of accuracy expressed by the following empirical formula,

$$(64) \quad 10^6 B = -906 + 6.87T = .0226T^2.$$

Chappuis's value for A_0 is 1.00906. The values indicated as being based on data by Chappuis and by Holborn and Austin, were obtained under the above named conditions. Some check computations for μ and η at 1 m. of Hg pressure based on quadrature methods and using Chappuis's constants unchanged showed excellent agreement with the values obtained using the modified constants of (63) and (64). To obtain values of C_p at zero pressure Holborn and Austin's data were used in conjunction with the change for one atmosphere indicated by the curves in Fig. 10. The results indicated as being based on Clausius's equation were obtained for zero pressure by a method analogous to that used in obtaining (27), and (28), and (61) and (62). Clausius's⁴⁶ equation and the numerical values of the constants are given in (65).

$$(65) \quad p = \frac{R\theta}{v-a} - \frac{c}{\theta(v+b)^2}$$

$$R = .003688,$$

$$a = .000843,$$

$$b = .000977,$$

$$c = 2.0935.$$

The resulting values for μ and η at zero pressure are

$$(66) \quad \mu_0 = \frac{\gamma - 1}{\gamma} \left(\frac{3v}{R'\theta} - \frac{a}{R} \right),$$

$$(67) \quad \eta_0 = \frac{2v(\gamma - 1)}{R'\theta^2}.$$

The curves of Fig. 9 furnished the desired values of γ . The value found by Searle⁸ was obtained through considering the application of Van der Waal's equation. The value by Cazin⁷ is an average of the four values .81, .82, .82 and 1.09 deg./atmo. which are obtainable from his results. The method is briefly described in the introduction. The first value is directly obtainable from his results. The other values are obtained indirectly. In obtaining his results for these three cases, Cazin had the larger chamber, into which the gas experimented on expanded from a smaller chamber, partially filled with the gas. In arriving at the above values, the rough assumption was made that the gas freely expanding was that in the smaller chamber in excess of the amount necessary to produce it in a pressure equal to the pressure existing in the larger chamber.

Note Regarding Disagreement of Values at Zero Pressure.—The high values of μ and η for $p = 0$ using Kammerlingh Onnes's equation (Fig. 12), are offset by the results based on the careful work of Chappuis and the work of Holborn and Austin and the results obtained with the aid of Clausius's equation. The difference arises from small variations in the p, v, θ relations. This disagreement might seem to cast doubt upon the values for the higher pressures. This is not necessarily the case, however, for with increasing pressure, as mentioned before, small errors in the p, v, θ relation become less effective due to the relative increase in size of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$.

Internal Work during Expansion.—As in the case with air, it is of interest to consider the relative magnitude of the internal work on expansion when compared with the external work. [35] gives this relation

for an infinitesimal, reversible, isothermal expansion. Values of $\frac{\Delta w_i}{\Delta w_g}$ are

included in the final columns of Table XVI. The results, excepting the value 5.71 for the critical point, have been plotted in Fig. 13. The platted points fall very closely on the smoothed curves. The effects of temperature and pressure are well shown. This plat incidentally shows very plainly the cause for the high values for γ at the higher pressures. In determining the isopiestic heat capacity of a gas, one neces-

sarily must consider the internal work of expansion, a factor which does not enter into the isometric heat capacity. Consequently there are relatively large values of γ , where the values of $\frac{\Delta w_1}{\Delta w_2}$ are relatively large.

This relation is further borne out by the striking similarity of the two plots.

Conclusions Regarding and μ , η , $\frac{\Delta w_1}{\Delta w_2}$ for CO_2 .—The following conclusions

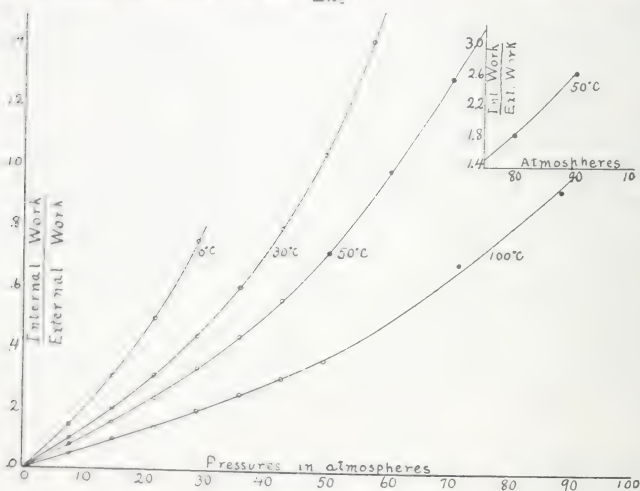


Fig. 13.

Variation with pressure of internal work for reversible, infinitesimal, isothermal expansions in CO_2 .

Results based on determinations of

C_p by Joule ●
 γ by Worthing ○

Conclusions for CO_2 for the regions considered may be drawn from the plots of μ , η and $\frac{\Delta w_1}{\Delta w_2}$.

1. For pressures up to about 60 or 70 atmospheres the free-expansion effect is less everywhere than the corresponding Joule-Kelvin effect. For the higher pressures the reverse is true.

2. For pressures up to about 60 or 70 atmospheres the values of μ and η decrease with increasing temperatures for the temperature interval 0° to 100° C. For sufficiently high pressures there is a reversal of this temperature effect.

3. μ for a given temperature is approximately independent of the pressure up to about 40 atmospheres. For higher pressures (excepting at 100° C.) it decreases with increasing pressure.

4. η for a given temperature is nearly constant with varying pressure up to about 30 atmospheres. With increasing pressures η first increases slightly, then decreases more rapidly.

5. There is general good agreement among the μ and η determinations based on the different experimental data.

6. The writer's computed values for μ at moderate pressures agree very well with the experimental values of Joule and Kelvin and with the values obtained by using Clausius's equation, but are consistently less than the results of Kester.

7. The writer's values for η show excellent agreement with the values to be computed on making use of Clausius's equation.

8. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ is greater for a given pressure the lower the temperature.

9. The ratio $\frac{\Delta w_1}{\Delta w_2}$ starts with zero values at zero pressure and increases with pressure, reaching a value of 5.71 at the critical point.

VII. SIGNIFICANCE OF A NOTICEABLE RELATION BETWEEN μ AND η FOR AIR AND FOR CO_2 .

It is to be noticed that the results for μ and η for air and CO_2 show some marked differences. Among them is the fact that η is greater than μ in air for the region considered, while the reverse is true for a large portion of the region considered in the case of CO_2 . A brief discussion of this fact may perhaps bring out the significance of this. Consider Fig. 14 in which POQ represents an isothermal platted on a (pv, p) diagram. Consider some gas to be in a state represented by O on the diagram and about to be expanded through a porous plug. On the diagram, the path representing the change will evidently proceed from O to some point to the left of mn .

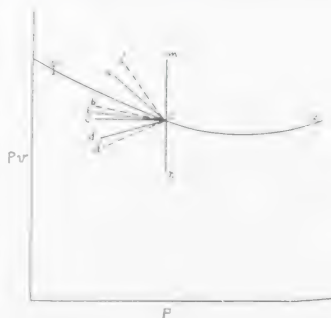


Fig. 14.

an isopiestic through O . In case the path should be along Ob , Oc or Od , cooling of the gas would occur and a positive Joule-Kelvin effect, as in air or in CO_2 , would be evidence. In case the path should be along Oe , heating of the gas would occur and a negative Joule-Kelvin effect as in hydrogen would be evidenced. The condition necessarily fulfilled in a porous plug expansion is

$$(68) \quad \Delta\epsilon + \Delta(pv) = 0.$$

The condition necessarily fulfilled in a free-expansion is

$$(69) \quad \Delta\epsilon = 0.$$

According to conditions, for instance whether in Fig. 14 the path proceeds from O into the upper left hand quadrant, along Oc , or into the lower left hand quadrant, we have respectively for the porous plug expansions

$$(70) \quad \Delta(pv) > 0, \quad \Delta(pv) = 0, \quad \Delta(pv) < 0.$$

For these cases we also have respectively

$$(71) \quad \Delta\epsilon < 0, \quad \Delta\epsilon = 0, \quad \Delta\epsilon > 0.$$

In the first case, where the path representing the porous plug expansion proceeds into the upper left hand quadrant and for which $\Delta\epsilon < 0$, the path for a free-expansion, in which $\Delta\epsilon = 0$, lies above that for the porous plug expansion. Hence, taking into account the signs of the effects, the free-expansion effect is less than the Joule-Kelvin effect.

In the second case, where the path representing the porous plug expansion proceeds along Oc and where $\Delta\epsilon = 0$, the path for a free-expansion also proceeds along Oc . Here the two cooling effects are equal.

In the third case, where the path representing the porous plug expansion proceeds from O into the lower left hand quadrant and for which $\Delta\epsilon > 0$, the path for a free-expansion in which $\Delta\epsilon = 0$, lies below that for the porous plug expansion. Here the free-expansion effect is greater than the porous plug effect. The converse of these statements is also true.

In the regions considered in air and in CO_2 we have for the most part portions of isothermals which when represented on diagrams as in Fig. 14 correspond to the portion PQ . In air where the Joule-Kelvin and free-expansion effects are both positive and the latter the greater, we have porous plug expansions and free-expansions whose paths would correspond respectively to Od and Od' . For CO_2 at the lower pressures, where the Joule-Kelvin and free-expansion effects are both positive and

the latter the smaller, the corresponding paths are Ob and Ob' . At somewhat higher pressures where the two effects are equal, the corresponding paths coincide and lie along Oc . At still higher pressures where the two effects are reversed, we have conditions existing as described above in air.

VIII. SUMMARY.

1. An expression has been developed which shows clearly the relation between the free-expansion effect γ and the ratio of the two heat capacities γ of a substance.

2. With the aid of γ data by Koch, $p v \theta$ data by Witkowski and an empirical equation of state by Kammerlingh Onnes, there have been computed values for the free-expansion effect η , the Joule-Kelvin effect μ and the ratio of the internal work to the external work for infinitesimal reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ for air at 0° C. and at -79.3° C. and for pressures up to 130 atmospheres.

3. With the aid of Kammerlingh Onnes's equation of state, there have been obtained experimentally by Maneuvrier's method values of γ for CO_2 at 0.0° , 31.0° , 50.0° and 98.5° C. and for pressures ranging from about 8 atmospheres to 57 atmospheres.

4. The approximate constancy of a new function γ' where γ' is defined by $p v' = \text{constant}$ —for CO_2 has been pointed out.

5. Values for the isometric heat capacity C_v , the isopiestic heat capacity C_p , μ , η and $\frac{\Delta w_1}{\Delta w_2}$ for CO_2 at 0° , 30° , 50° and 100° C. and for pressures—making use of C_v data by Joly—up to 90 atmospheres have been computed.

6. The results of the present work have been shown to be generally in good agreement with the experimental results of others.

7. A discussion has been presented in which certain characteristics of the expansions of air and of carbon dioxide through a porous plug and into a vacuum are considered.

The conclusions reached regarding the variations of the various quantities considered will be found summarized at the close of the different subdivisions of the present paper.

In conclusion, I wish to express my sincere thanks to Mr. R. E. Miller for care shown in the construction of the apparatus, to Mr. C. E. Guthe, Jr., for efficient aid given in the experimental work, and especially to Dr. K. E. Guthe for his kindly interest and helpful suggestions.

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ANN ARBOR, MICH.,

March, 1911.

IX. BIBLIOGRAPHY.

1. Gay-Lussac: *Mém. d'Arcueil*, I, 1807; Mach's *Die Principien der Wärmelehre*; *The Free-expansion of Gases*, ed. by J. S. Ames.
2. Mayer: *Lieb. Ann.*, 42, p. 1, 1842.
3. Joule: *Phil. Mag.* (3), 26, 369, 1845; *Sci. Papers*, I., p. 172; *The Free-expansion of Gases*, ed. by J. S. Ames, p. 17.
4. Thompson and Joule: *Phil. Trans.*, 144, p. 321, 1854; Joule's *Sci. Papers*, II., p. 247; Kelvin's *Sci. Papers*; *The Free-expansion of Gases*, ed. by J. S. Ames, p. 55.
5. Regnault: *Hirn's Theorie Mechanique de la Chaleur*, I., p. 148; O. D. Chwolson's *Lehrbuch der Physik*, III., p. 540.
6. Hirn: *Theorie Mechanique de la Chaleur* (3 ed.), II., p. 387.
7. Cazin: *Ann. de Chim. et de Phys.* (4), 19, p. 5, 1870; *Phil. Mag.* (4), 40, pp. 81, 197, 268, 1870.
8. Searle: *Proc. Camb. Phil. Soc.*, 13, p. 241, 1906.
9. Thompson and Joule: *Phil. Trans.*, 143, p. 357, 1853; 144, p. 321, 1854; 152, p. 579, 1862; Joule's *Sci. Papers*, II., p. 247; Kelvin's *Math. and Phys. Papers*, II., p. 387; *The Free-expansion of Gases*, ed. by J. S. Ames.
10. Rose-Innes: *Phil. Mag.* (5), 45, p. 227, 1898; (5), 50, p. 251, 1900; (6), 2, p. 130, 1901; (6), 3, p. 131, 1901.
11. Berthelot: *Trav. et Mem. du Bur. Int.*, 13, p. 133, 1903.
12. Buckingham: *Bul. Bur. Stand.*, 3, p. 237, 1907; *Phil. Mag.* (6), 15, p. 526, 1908.
13. Natanson: *Wied. Ann.*, 31, p. 502, 1887.
14. Kester: *PHYS. REV.*, 21, p. 260, 1905.
15. Rudge: *Phil. Mag.* (6), 18, p. 159, 1909.
16. Dalton: *Proc. Konink. Akad. Wetensch. Amsterdam*, 11, p. 874, 1909; *Comm. No. 109C*, *Phys. Lab. Leiden*.
17. Witkowski: *Rozprawy Krak. Akad. Math. Naturw. klasse*, 23 u. 32; *Phil. Mag.* (5), 41, p. 288; 42, p. 1, 1896; *Bul. Acad. Sc. Cracovie*, p. 282, 1898.
18. Olszewski: *Bul. Acad. Sc. Cracovie*, 9, p. 453, 1901; *Ann. d. Phys.* (4), 7, p. 818, 1902; *Krak. Anz.*, p. 792, 1906; *Phil. Mag.* (6), 13, p. 723, 1907.
19. Berthelot: *C. R.*, 130, p. 1379, 1900.
20. Porter: *Phil. Mag.* (6), 11, p. 554, 1906; 19, p. 888, 1910.
21. Lummer: *Phys. Zeit.*, 7, p. 864, 1906.
22. Dickson: *Phil. Mag.* (6), 15, p. 126, 1908.
23. Dalton: *Proc. Konink. Akad. Wetensch. Amsterdam*, 11, p. 863, 1909; *Comm. No. 109A*, *Phys. Lab. Leiden*.
24. Koch: *Ann. d. Phys.* (4), 26, p. 551; 27, p. 311, 1908.
25. Kammerlingh Onnes: *Comm. No. 47*, *Phys. Lab. Leiden*.
26. Witkowski: *Bul. Acad. Sc. Cracovie*, p. 138, 1899; *Fort. d. Phys.*, II., p. 664, 1899.
27. Joly: *Proc. Roy. Soc. Lond.*, 45, p. 33, 1888; 48, p. 440, 1890.
28. Lussana: *Nuov. Cim.* (3), 36, pp. 5, 70, 130, 1894; (4), 2, p. 327, 1895; *Fort. d. Phys.*, II., p. 367, 1894; II., p. 414, 1895.
29. Amagat: *Ann. Chim. et Phys.* (6), 29, p. 505, 1893; *The Laws of Gases*, ed. by Barus.
30. Bakker: *Zeit. f. Phys. Chem.*, 14, p. 672, 1894; 17, p. 171; *Jour. de Phys.* (3), 7, p. 152, 1898; *PHYS. REV.*, 31, p. 589, 1910.
31. Amagat: *C. R.*, 121, p. 863, 1895; *Jour. de Phys.* (3), 5, p. 114, 1896.
32. Joly: *Proc. Roy. Soc. Lond.*, 55, pp. 390, 392, 1894; *Phil. Trans.*, 185A, pp. 943, 961, 1894.
33. Lussana: *Nuov. Cim.* (4), 3, p. 92, 1896; *Fort. d. Phys.*, II., p. 344, 1896.
34. Jamin and Richard: *C. R.*, 71, p. 336, 1870.
35. Assman: *Pogg. Ann.*, 85, p. 1, 1852. Hartmann: *Ann. d. Phys.* (4), 18, p. 252, 1905.
36. Lummer and Pringsheim: *Wied. Ann.*, 64, p. 553, 1898.
37. Maneuvrier: *Ann. Chim. et Phys.* (7), 6, p. 321, 1895.
38. Capstick: *Sci. Prog.*, 3, p. 19; *Phil. Mag.* (6), 2, p. 649, 1901.

39. Jeans: *Phil. Mag.* (6), 2, p. 639, 1901; *Dynamical Theory of Gases*, p. 378, and Chap. XVI.
40. Reech: *Buckingham's Theory of Thermodynamics*, p. 81.
41. Kamerlingh Onnes: *Arch. Neerl.* (2), 6, 46, 874, 1901 (Comm. No. 74, Phys. Lab. Leiden).
42. Holborn and Austin: *Abhandl. Phys. Tech. Reichs.*, 4, p. 133, 1907; *Phys. Rev.*, 21, p. 207, 1905.
43. Swann: *Proc. Roy. Soc. Lond.*, 82, p. 137, 1910.
44. Keesom: *Proc. Konink. Akad. Wetensch. Amsterdam*, pp. 391, 533, 616; *Diss. Leiden*, 1904; *Comm. No. 88, Phys. Lab. Leiden*.
45. Chappuis: *Trav. et Mem. du Bur. Int.*, 13A, 66S, 1903; *Jour. de Phys.* (4), 3, p. 835, 1904; *Fort. d. Phys.*, I., p. 226, 1903.
46. Clausius: *Wied. Ann.*, 6, p. 117, 1880.

ERRATA AND ADDENDA.

Page 259. To enable one to locate properly points platted in Fig. 12 in the paper by A. G. Worthing on Some Thermodynamic Properties of Air and of Carbon Dioxide, the following table is given:

TABLE II. The γ and γ data by Worthing.			
in Atmos.	in ° C.	in Deg. Atmos.	in Deg. Atmos.
Results of Joule and Thomson.			
1-0	4.0	1.897	
	83.5	1.020	
	51.9	.883	
	91.8	.948	
	96.0	.639	
Result of Cazin.			
1-5	10		.88
Result of Natanson.			
	19.7	1.18	
Results of Kester.			
1-40	.6	1.112	
	20.4	1.173	
	39.5	1.037	
	59.5	.948	
	79.5	.868	
	96.6	.786	
Result of Searle.			
5-10	0		.63
Results of Worthing.			
0	0	1.873	1.265
	30	1.065	.975
	50	.910	.830
	100	.595	.540
Results based on data by Chappuis and by Holborn and Austin.			
0	0	1.290	1.125
	30	1.108	.970
	50	.960	.850
	100	.575	.480
Results based on Clausius's equation and γ data by Worthing.			
	0	1.36	1.22
	30	1.06	.96
	50	.90	.81
	100	.61	.55

RESIDUAL RAYS OF SELENITE

By H. M. RANDALL.

In a recent paper J. Koch¹ has reported the results of a new determination of the wave-length of the residual rays ("Reststrahlen") from selenite. The method makes use of a Jamin interferometer by means of which a direct comparison is made between corresponding numbers of interference bands due to the "Reststrahlen" and to the sodium line $\lambda = 0.58948 \mu$ (*vacuo*). The following results were obtained:

- (1) $\lambda = 8.6795 \mu$ (*vacuo*) (mean of 10)
- (2) $\lambda = 8.6770 \mu$ (*vacuo*) (mean of 5)
- (3) $\lambda = 8.6789 \mu$ (*vacuo*) (mean of 5)

Mean $\lambda = 8.6787 \mu$ (*vacuo*)

The relatively close agreement of the various values is interesting and raises the question as to whether other methods will yield the same result; that is, whether the "Reststrahlen" from selenite may be employed as a standard wave-length in the infra-red region. Energy-curves of this radiation have been obtained accordingly by using both the grating and the prism method. As these methods are familiar, the experimental details will be sufficiently indicated by the accompanying diagram, Fig. 1. *S*, the source of the radiation, is a 220-volt Nernst lamp, whose image is focused by the silvered mirror *M* upon the slit *S'*, of the mirror spectrometer after three reflections at the polished selenite surfaces *g*, the angle of incidence being about 45° . *M*₁ and *M*₂ are silvered mirrors 10 cm in diameter and of 50 cm focal length, while *L* is a plane Rowland grating with 40 lines per mm. The spectrometer was made by Fuess and has been previously described.² The linear thermopile *T* was of the Paschen type³ and is used in connection

¹ *Annalen der Physik*, **26**, 974, 1908.

² E. Giesing, *Annalen der Physik*, **22**, 333, 1907.

³ F. Paschen, *ibid.*, **33**, 736, 1910.

with a Paschen galvanometer, with which a deflection of 1 mm corresponded to a current of 0.7×10^{-10} amperes, the scale being approximately 2.5 m from the galvanometer. The deflections of the galvanometer were proportional to the current throughout the length of the scale. The slits S and S' were kept equal and gradually increased in width till sufficient radiation passed through to give satisfactory deflections of the galvanometer. A relatively wide slit, 1.7 mm, was found necessary. This corresponds to a spectral region of about 800 Å.U. The wave-length, λ , is given by the equation ($\lambda = C \sin \theta$), C being determined by using the *He* line S λ 5875.870 in the 30th and 40th orders. C was found to be 504817 Å.U.

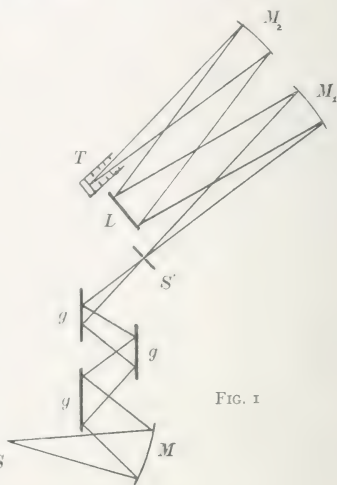


FIG. 1

Fig. 2 represents the energy-curves to the right and left of the undeviated image, the abscissas are the spectrometer readings and the ordinates the galvanometer-throws when the shutter before the slit S is removed. The wave-length corresponding to the center of mass of the triangles is $\lambda = 86940$ Å.U. (*vacuo*). A second independent determination gave $\lambda = 86950$. These values are in accord with that of Aschkinass¹ which was 8.69μ .

The grating was then replaced by a fluorite prism, and the slits were narrowed to 0.28 mm. In this case the slit-width corresponded approximately to 180 Å.U. The curves of Fig. 3 were obtained with this arrangement. The observed throws of the galvanometer are indicated by the points of the lower curve. These have been increased by multiplying by the proper factor to

¹ *Annalen der Physik*, 1, 42, 1900.

compensate for the absorption of the fluorite,¹ which is large in this region, and the upper curve represents the values which would have been obtained had there been no absorption. This curve gives $\lambda = 86785$ Å.U. (*vacuo*) for the wave-length corresponding to the center of mass of the triangle. This is also quite accurately the value of the wave-length corresponding to the maximum of the curve. It will be noticed that this result is in close agreement with those of Koch, indicating the correctness of the determinations of Paschen on the dispersion and absorption² of fluorite in this

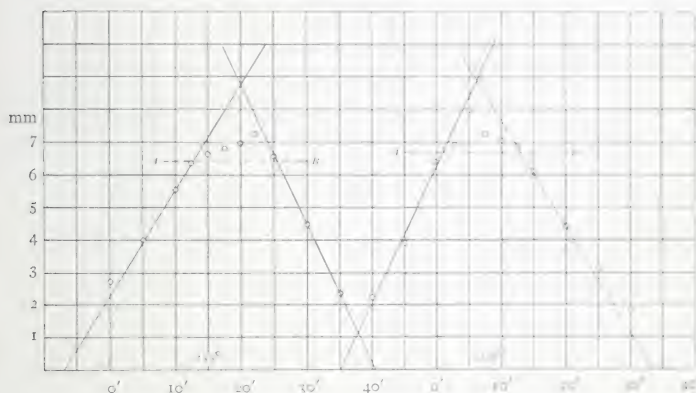


FIG. 2

region. While the value obtained by the grating is perceptibly larger than that given by the prism, due possibly to the alterations in the energy-distribution of the spectrum which a grating may introduce, it is interesting to observe that the wave-lengths obtained from those parts of the bands carrying the maximum energy are nearly the same in the two cases, being in fact also in close agreement with the values of Koch. Thus, if the values of λ are obtained from the intersections of the lines AB with the curves, the following results are obtained:

¹ F. Paschen, *Sitzungsberichte der K. preuss. Akademie der Wissenschaften*, **1**, 417, 1899.

² F. Paschen, *Annalen der Physik*, **53**, 301, 812, 1894.

Grating $\lambda = 86793 \text{ \AA.U. (vacuo)}$
 Prism $\lambda = 86770 \text{ \AA.U. (vacuo)}$
 while from Koch $\lambda = 86787 \text{ \AA.U. (vacuo)}$.

It is to be noted also that the approximate breadth of the band in the case of the prism is 0.5μ and in the case of the grating 0.6μ , values which are in substantial agreement with the value 0.5μ obtained by Koch from visibility-curves.

While the values from the energy-curves by either of the methods here used may be repeated under definite conditions with variations not exceeding $20 \text{ \AA.U.}$, still the fact that the different methods

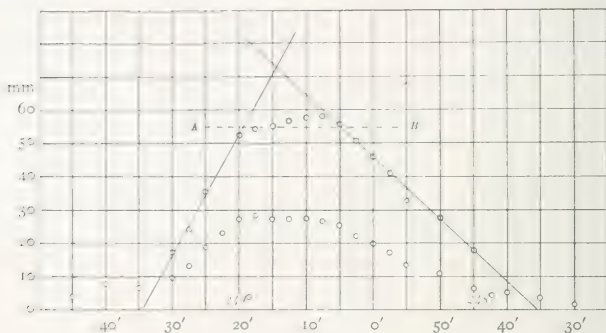


FIG. 3

give appreciably different results and also the fact that the band seems to have a rather broad maximum make it unsuitable for a standard of wave-length. In fact, the form of this somewhat broad maximum suggests the possibility of a double maximum for the residual rays of selenite in this region. The data do not warrant, however, any positive conclusions in this respect.

These data were obtained in the Physical Laboratory of the University of Tübingen and the writer wishes to express here his deep obligations to its director, Professor F. Paschen.

PHYSICAL LABORATORY
 UNIVERSITY OF MICHIGAN

August 1911

THE ELASTIC PROPERTIES OF BISMUTH WIRES.¹

BY J. E. HARRIS.

A MOST striking deviation from the laws of elasticity was first observed a few years ago by Guthe² and investigated by him³ and by Sieg⁴ in wires of platinum-iridium alloys. They found that the period of torsional vibration for these wires was by no means constant, but that it decreased rapidly with the amplitude of vibration. The greatest percentage of decrease was found in the smaller amplitudes, the periods seeming to approach a maximum constant value at the larger amplitudes. The logarithmic decrement, starting with the large amplitude, at first increased slowly to a maximum value and then decreased much more rapidly as the amplitude of vibration decreased. The previous treatment of the wire seemed to influence its behavior greatly. After allowing the wire to rest for a long time, or after annealing the wire by heating it to a red heat by means of an electric current, the peculiar properties were not nearly so pronounced as when the wire had just previously been vibrated torsionally for some time. It was also observed that when the wire was kept in vibration for some time at a constant amplitude, the period gradually increased until it finally approached a maximum constant value.

The fact that the previous history and treatment of the wire seemed to influence its behavior to such an extent led to the assumption that the effect was in some way due to the molecular structure of the wire. Since the platinum-iridium alloys are very brittle, it was suggested that perhaps other wires having this same quality of brittleness might show something of the same properties. For this reason, it was decided to investigate the behavior of bismuth wires. This was done and as has been announced by Guthe⁵ and the author, the bismuth wires did show the same large decrease in period and logarithmic decrement with decrease in amplitude.

This paper gives the results of the investigations that have been carried on in the past year with bismuth wires.⁶

¹ This investigation was carried out with the aid of a grant from the Elizabeth Thompson Science fund.

² K. E. Guthe, Proc. Iowa Academy of Science, 15, p. 147, 1908.

³ K. E. Guthe and L. P. Sieg, PHYSICAL REVIEW, Vol. 30, No. 4, 1910.

⁴ L. P. Sieg, PHYSICAL REVIEW, Vol. 31, No. 4, 1910.

⁵ PHYSICAL REVIEW, Vol. 32, p. 228.

⁶ The bismuth wires used in these investigations were obtained from Hartman & Braun. They were made from pure, electrolytically deposited bismuth.

II. APPARATUS.

The apparatus was similar in most respects to that described by Guthe and Sieg¹ in their investigations with the platinum iridium wires. A large circular scale was used of such dimensions that each degree of amplitude measured about 2 cm. on the circumference of the scale. Each end of the wire was soldered into a brass cylinder. For the purpose of soldering the wires, it was found necessary to mix some bismuth with the solder in

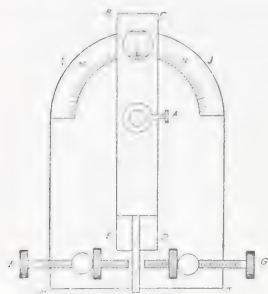


Fig. A.

order to lower its melting point to a temperature below that for bismuth, the melting point of pure bismuth itself being lower than that of the solder. The upper cylinder was clamped in a device shown in the accompanying diagram. The sketch gives a view at right angles to the axis of the wire. The cylinder to which the upper end of the wire is soldered is held in place by the set-screw *A*. The flat piece of iron *BCDE* carrying the cylinder is free to rotate about the axis of the wire as a center of rotation. By pushing this first one way and then the other, the wire could be made to vibrate. By means of the set-screws *F* and *G*, the angle through which the wire was twisted could be regulated at will. By setting these screws, the wire could also be made, if desired, to vibrate at constant amplitude. The part *HIJK* is a fixed piece of iron and has at one end of it the circular scale *mn*. By means of this scale, the angle through which the wire is being twisted can be determined.

The cylinder attached to the lower end of the wire was turned in such a way as to leave at its lower end a flat disk 5.58 cm. in diameter. Over the stem part could be slipped cylinders of various masses and diameters, so that the mass and moment of inertia of the vibrating system could be varied as desired. A very thin piece of plane parallel glass, silvered on both sides and fastened vertically to the lower surface of the vibrating disk, served for the reflection of light from an arc lamp to the scale. The lower cylinder was hung in a large beaker made of clear glass, the top of the beaker being covered with a piece of cardboard having a hole in the center through which the wire could pass. This arrangement was made necessary, especially in those observations in which a light suspended weight was used, because it was found that the air currents in the room interfered materially with the observations. The beaker was large

¹ Loc. cit.

enough so as not to introduce any damping effect. A cross-wire placed in a beam of light from an arc lamp was focused on the scale after reflection by the mirror by means of a lens.

The periods of vibration were obtained with the aid of a Morse recorder, one of the electromagnets of the recorder being connected to a relay which in turn was connected to a clock beating seconds, the other electromagnet being connected to the apparatus used for determining the time of the passage of the cross-wire through the point of rest. By measuring the distance between the marks on the tape, an accurate determination of the time of each passage of the cross-wire through the point of rest could be obtained.

In the earlier observations, instead of determining the time of passage of the cross wire through the point of rest by means of a tap-key, a selenium cell was placed in the position occupied by the spot of light reflected by the mirror when the vibrating system was at rest. The cell, which was very sensitive, having a resistance of 198,000 ohms in the dark and only 8,000 ohms in direct sunlight, was placed in series with a two-thousand ohm relay and both connected in a 220-volt circuit. The relay was so adjusted that when the light from the mirror passed over the cell in series with the relay, the decreased resistance of the cell would permit enough current to pass to close the relay, which, in turn closed a circuit containing one of the electromagnets of the recorder, thus giving a mark on the tape. For the larger amplitudes, the entire surface of the cell (about $5 \times 2\frac{1}{2}$ cm.) was exposed to the action of the light. However, as the amplitudes of vibration decreased, the spot of light remained for a continually lengthening period of time on the surface of the cell, so that the mark on the tape could no longer be given at the time of the passage of the spot of light over the middle of the cell but before it reached the middle. For this reason, two pieces of card-board were so arranged that they could be closed in from the ends, thus leaving a continually decreasing portion of the cell exposed to the action of the light. It was found that the slit could be narrowed down in this manner until it was considerably less than a centimeter in width. Even this was too wide for amplitudes less than 20° so that when the amplitude had decreased to this point, the records of the passages of light were obtained by means of a tap-key. Unfortunately, due to the passage of too much current through the cell in one of the observations, the sensitiveness was decreased to such an extent that it could no longer be used, and a tap-key had to be substituted in the observations taken thereafter.

III. METHOD OF PROCEDURE.

The object of the first experiment attempted was to determine the way in which the wire behaved as the initial amplitudes of successive observations were gradually increased. For this purpose, a series of experiments was carried on with two different wires, one of .25 mm. diameter and the other .5 mm. diameter, in each case beginning with an observation in which the initial amplitude was small and increasing the amplitude in each succeeding observation. The amplitudes were increased in each case until the elastic limit of the wire was very nearly reached. For all the experiments, a smooth period amplitude curve could be obtained, but when the curves were compared, no definite relation could be obtained. The curves for experiments, in which the initial amplitude was large, would sometimes be above and sometimes below those in which the initial amplitude was small. This was probably due to the different treatment of the wire on different occasions. It was necessary to adjust the relay in series with the selenium cell as the wire was being vibrated in order to bring it up to the desired initial amplitude and sometimes this adjustment was difficult to bring about, especially if the light from the arc happened to be a little variable. For this reason, it was necessary to keep the wire in vibration much longer in some experiments than in others.

From these results, it became evident that some method of procedure, would have to be found by which more definite results could be obtained. In Sieg's¹ work, the method was tried of keeping the wire in constant vibration for some time at the maximum amplitude at which it was desired to begin the experiment and then taking a series of observations as the wire came to rest. It was found that if this experiment was repeated at once without the preliminary treatment, the period amplitude curves for the two sets of readings coincided exactly, indicating that the wire, for the time being at least, had been put in a definite state.

A series of experiments were performed to see if in this respect the bismuth wire behaved like the platinum-iridium wire.

1. *Comparison of Two Series of Observations taken One Immediately After the Other.*—In order to determine definitely the effect of the previous treatment of the wire, two series of observations were taken one immediately after the other. In this experiment, a wire was used that had been used in the experiments mentioned above. The wire had, however, been allowed to rest several days before these experiments were performed. The wire was made to vibrate in each case through an initial amplitude of about 85° and the observations taken as the system

¹ Loc. cit.

came to rest. In this and all other experiments with the bismuth wires, we are limited to small amplitudes compared to those used in the platinum-iridium wires, because of the low elastic limit of the wire. By period in this and in subsequent experiments is meant the period of half a complete vibration. The results for the two experiments are given in Table I., *A* being for the first and *B* for the second series of readings.

TABLE I.

Length of wire, 106 cm. Diam., .5 mm. Moment of inertia, 626 g. cm². Temp., 23°. Initial amplitude, 86°.3.

No. of Swing.	<i>A</i>		<i>B</i>	
	Period.	Amp.	Period.	Amp.
5	3.223	73.4	3.224	74.0
10	3.219	63.1	3.221	63.3
15	3.216	54.0	3.217	54.3
20	3.213	46.7	3.215	45.8
25	3.211	40.0	3.213	40.5
30	3.209	34.6	3.210	34.7
35	3.206	30.0	3.207	30.2
40	3.203	26.1	3.205	26.3
45	3.201	22.8	3.203	23.0
50	3.199	19.8	3.201	20.0
55	3.197	17.4	3.200	17.5
60	3.195	15.3	3.198	15.4
65	3.194	13.5	3.196	13.5
70	3.192	11.9	3.194	11.8
75	3.191	10.6	3.193	10.5
80	3.189	9.3	3.192	9.2
85	3.188	8.4	3.190	8.3
90	3.187	7.5	3.189	7.4
95	3.187	6.7	3.188	6.6
100	3.186	6.1	3.187	5.7
105	3.185	5.4	3.187	5.1
110	3.185	4.9	3.186	4.7
115	3.184	4.4	3.185	4.3
120	3.183	3.8	3.185	3.7

The results of this experiment are shown graphically in Fig. 1, the amplitudes being plotted as abscissæ and the periods as ordinates. That the first experiment has had a marked effect on the second is evident from the position of the two curves. The curve for the second experiment lies above that for the first. It will be seen that the second curve in shape is very similar to that of the first. It seems that the effect of the first experiment on the second was merely to displace the curve upward. This effect is due to the so-called "elastic fatigue" in the wire.

2. *Behavior of the Wire when Vibrated at Constant Amplitude.*—In this experiment, several series of observations were taken at different amplitudes to determine whether or not the period remained constant when

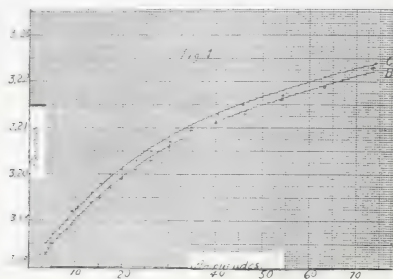


Fig. 1.

the wire was kept vibrating at constant amplitudes. By adjusting the set screws *F* and *G* (see diagram) and moving the lever from one set screw to the other at the end of each swing, the wire could be kept vibrating through any desired amplitude and this amplitude kept constant

TABLE II.

Length of wire = 106 cm. Diam. = .5 mm. Moment of inertia = 626 g. cm².
A. Amplitude = 65°.2.

Coincidence.	Intervals.	No. of Vibrations.	Period.
21.21			
53.42	32.21	10	3.221
108.29	87.08	27	3.225
205.13	183.92	57	3.227

After 20 minutes.

1.56			
85.57	84.01	26	3.231
130.78	129.22	40	3.231
260.07	258.51	80	3.231

B. Amplitude = 93°.5.

37.70			
79.63	41.93	13	3.225
115.12	77.42	24	3.226
192.61	154.91	48	3.227

After 20 minutes.

1.54			
62.96	61.42	19	3.233
224.65	223.11	59	3.233
337.82	336.28	104	3.233

within one or two degrees. Only two of the experiments performed are given here for the reason that all of them gave practically the same results. Two series of observations were taken in each case, the first just after the amplitude desired had been reached, and the second, after the wire had been kept in vibration for 20 minutes. The results are shown in Table II.

It will be seen from the above experiments, that the period of vibration increases when the system is made to vibrate at a constant amplitude; that the period of vibration very rapidly approaches a maximum value; and that this maximum value has apparently been reached after an interval of 20 minutes. To make sure of this latter point, the wire was vibrated for twenty minutes, an observation taken and then the wire vibrated for an hour and another observation taken. The period obtained was the same as that obtained after the twenty-minute interval. That a part of the adjustment of the wire takes place while the wire is being vibrated to bring it up to the maximum amplitude is shown by the above tables. In observation A, where the wire was brought to its maximum amplitude by larger steps than in B, we have a larger variation in the period in the first 50 vibrations than in the corresponding interval in the second observation.

3. *Effect of Continued Vibrations on the Period Amplitude Curve.*—To show this effect, a wire that had not been used before was taken and after allowing it to hang in place for a day, three series of observations were

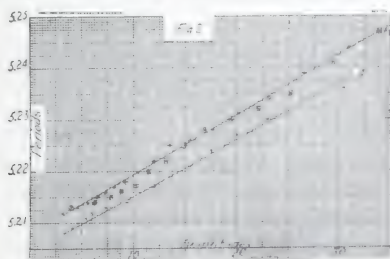


Fig. 2.

taken. In the first, the wire was brought up to the desired amplitude with as few preliminary swings as possible and a series of observations taken as the wire came to rest. In the second experiment, the wire was kept vibrating for a period of about thirty minutes at the same amplitude as that at which the first experiment was begun before taking the series of observations. The third experiment consisted in repeating the first experiment immediately after the second had been completed. The results appear in Table III.

TABLE III.

Length of wire, 103.6 cm. Diam., .25 mm. Moment of inertia, 133 g. cm².

No. of Swing.	Exp. A. Initial Amp. 35° o. Temp. 20° 5.		Exp. B. Initial Amp. 35° .4. Temp. 20° .5.		Exp. C. Initial Amp. 38° o. Temp. 20° .8.	
	Period.	Amplitude.	Period.	Amplitude.	Period.	Amplitude.
5	5.236	30.4	5.244	30.8	5.247	33.8
10	5.234	26.3	5.239	26.5	5.241	29.3
15	5.230	22.9	5.234	23.2	5.235	25.4
20	5.227	20.0	5.231	20.1	5.232	22.1
25	5.224	17.5	5.228	17.6	5.230	19.3
30	5.221	15.5	5.226	15.3	5.228	16.9
35	5.219	13.6	5.225	13.5	5.225	14.9
40	5.217	11.9	5.222	11.9	5.222	13.1
45	5.216	10.6	5.220	10.5	5.220	11.5
50	5.214	9.3	5.218	9.2	5.217	10.2
55	5.213	8.3	5.217	8.2	5.216	9.0
60	5.213	7.3	5.216	7.3	5.215	7.9
65	5.213	6.5	5.215	6.5	5.214	7.0
70	5.212	5.9	5.214	5.7	5.214	6.3
75	5.211	5.3	5.213	5.1	5.214	5.6
80	5.210	4.7	5.213	4.6	5.214	5.0
85	5.209	4.1	5.213	4.0	5.213	4.4
90	5.209	3.7	5.213	3.6		
95	5.208	3.3	5.212	3.2		

The results of these experiments are shown graphically in Fig. 2, curves *A* and *B*. In this figure, the amplitudes are plotted as abscissæ and the periods as ordinates. In curve *A*, we have the results of experiment *A* plotted and in curve *C*, the results of *B* and *C*. It will be noticed that in all three cases the points lie very nearly in a straight line. The straight line marked *A* lies somewhat below that marked *B* but the slope of the two lines is about the same. This would indicate that the continued vibration which the wire underwent, before the observations in *B* were taken, has increased the period for all the amplitudes from the maximum to the lowest for which readings were taken. Curve *B* shows that the points for experiments *B* and *C* lie very nearly on the same straight line.

To determine whether or not the results are the same when the wire is kept in continual vibration at a larger amplitude, the experiment was repeated using an initial amplitude of about 190°. This amplitude is slightly under that permitted by the elastic limit of the wire.

The results of these experiments are shown in Fig. 3. The results are quite similar to those found in the preceding experiment. Fig. 3 shows the curve for experiments *B* and *C* lying above that for *A* and the curves for *B* and *C* coinciding. These experiments indicate that the

wire for the time being at least has been put in a definite state. It was determined, as a result of these experiments, that all subsequent series of observations should be taken after the wire had been kept in continuous vibration for a period of from twenty minutes to half an hour.

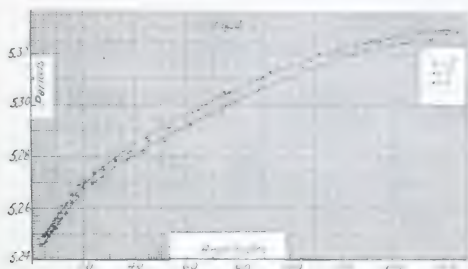


Fig. 3.

TABLE IV.

Length of wire, 106 cm. Diam., .25 mm. Moment of inertia, 133 g. cm².

No. of Swing.	Exp. A. Initial Amp. 184° 8. Temp. 23° 2.		Exp. B. Initial Amp. 192° 5. Temp. 23° 2.		Exp. C. Initial Amp. 195° 0. Temp. 23° 2.	
	Period.	Amplitude.	Period.	Amplitude.	Period.	Amplitude.
5	5.326	156.5	5.328	161.5	5.329	165.8
10	5.321	127.9	5.325	131.7	5.235	135.8
15	5.315	105.5	5.318	108.2	5.320	111.8
20	5.306	87.6	5.311	89.7	5.313	92.2
25	5.297	73.1	5.305	74.7	5.305	76.8
30	5.292	61.3	5.297	62.2	5.298	64.4
35	5.286	51.6	5.291	52.5	5.291	53.9
40	5.282	43.7	5.287	44.2	5.286	45.7
45	5.279	37.2	5.281	37.6	5.282	38.6
50	5.276	31.8	5.279	32.0	5.278	32.9
55	5.272	27.1	5.276	27.3	5.275	28.1
60	5.270	23.3	5.274	23.6	5.274	24.2
65	5.268	20.3	5.271	20.5	5.270	20.8
70	5.265	17.4	5.269	17.6	5.269	17.9
75	5.262	15.2	5.265	15.3	5.265	15.5
80	5.258	13.2	5.261	13.3	5.262	13.5
85	5.256	11.6	5.258	11.6	5.261	11.8
90	5.254	10.3	5.256	10.1	5.258	10.4
95	5.252	9.0	5.254	8.8	5.256	9.0
100	5.251	7.9	5.253	7.8	5.254	7.9
105	5.249	6.8	5.252	6.8	5.251	7.0
110	5.247	6.0	5.251	6.3	5.250	6.1
115	5.247	5.2	5.250	5.6	5.250	5.3
120	5.246	4.6	5.250	4.9	5.249	4.7
125	5.246	4.1	5.249	4.3		
130	5.246	3.6				

The logarithmic decrements for the various amplitudes were worked out for the above experiment and these logarithmic decrements plotted against the corresponding amplitudes in order to determine the effect of continued vibration on the logarithmic decrement. The results are given in Table V.

TABLE V.

Exp. A.			Exp. B.			Exp. C.		
No. of Swings.	Log. Dec.	Amp.	No. of Swings.	Log. Dec.	Amp.	No. of Swings.	Log. Dec.	Amp.
8	.0178	156.5	8	.0179	161.5	8	.0174	165.8
10	.0170	127.9	10	.0174	131.5	10	.0171	135.8
10	.0166	105.5	10	.0167	108.3	10	.0168	111.8
10	.0160	87.6	10	.0161	89.7	10	.0163	92.2
10	.0155	73.1	10	.0159	74.7	10	.0156	76.8
10	.0151	61.3	10	.0153	62.2	10	.0154	64.4
10	.0147	51.6	10	.0148	52.5	10	.0149	53.9
10	.0142	43.7	10	.0144	44.2	10	.0145	45.7
10	.0138	37.3	10	.0140	37.6	10	.0143	38.6
20	.0137	31.8	20	.0136	32.0	20	.0139	32.9
20	.0132	27.1	20	.0132	26.3	20	.0135	28.1
20	.0128	23.3	20	.0130	23.6	20	.0132	24.2
20	.0126	20.3	20	.0127	20.5	20	.0129	20.9
20	.0123	17.6	20	.0125	17.6	20	.0127	17.9
20	.0122	15.3	20	.0124	15.3	20	.0123	15.5
20	.0116	13.2	20	.0121	13.3	20	.0119	13.5
20	.0114	11.6	20	.0120	11.6	20	.0118	11.8
20	.0111	10.3	20	.0116	10.1	40	.0117	10.4
20	.0115	7.9	40	.0108	7.8	40	.0115	7.9
20	.0113	6.0	40	.0106	5.6	40	.0112	6.1
20	.0113	4.6				40	.0109	4.7
20	.0113	3.6						

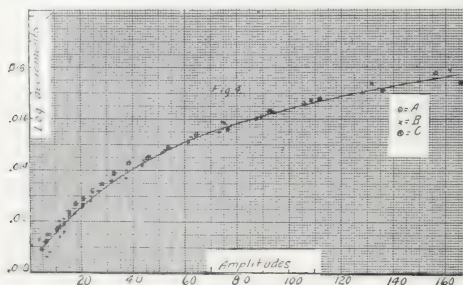


Fig. 4.

In the above table, the first, fourth and seventh columns give the number of swings used in determining the mean logarithmic decrement. The results have been plotted and are shown in Fig. 4. It is seen that

In Fig. 5 the curves *A*, *B*, *C* and *D* are the period-amplitude curves for experiments *A*, *B*, *C* and *D*. It will be observed that the periods in each successive curve are higher than the corresponding periods of the next preceding curve. These curves are in many respects different from those obtained by Guthe and Sieg with the platinum-iridium wires. In the corresponding experiment with the platinum-iridium wires, while

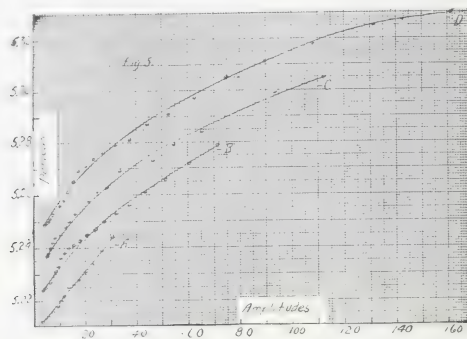


Fig. 5.

the curves for the experiments performed with the large initial amplitudes lay above those for the small amplitudes, the curves seemed to start from a common point, which is not the case with the curves for the bismuth wires. It was also noticed in the experiments with the platinum-iridium wires that at large amplitudes the periods approached a certain maximum value. In this experiment and in all others with the bismuth wires, it was found that, while the curves became less steep with larger amplitudes, no maximum was reached. However, in the case of the bismuth wires, the observations are limited by the low elastic limit to amplitudes that are very low compared to those used with the platinum-iridium wires, so that it may be that the curves shown in the figure correspond to those portions of the curves for the platinum-iridium wires, where the rate of increase in the period is greatest. Also it must be remembered that in the experiment with the platinum-iridium wires the wires were not kept in continuous vibration before taking the observations.

It will be noticed that the curves for the bismuth wires have very much the same shape and slope. The chief difference in the successive curves seems to be one of displacement, the direction of displacement being upward for the larger amplitudes.

The Logarithmic Decrement.—The logarithmic decrements for these

observations were computed and plotted as ordinates with the corresponding amplitudes as abscissæ. The results are given in Table VII, and the curves shown in Fig. 6. The curves *A*, *B*, *C* and *D* correspond to experiments *A*, *B*, *C* and *D*.

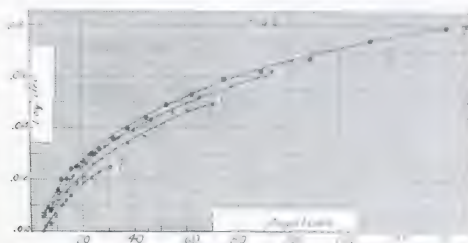


Fig. 6.

It is found that in all the curves there is a marked decrease in the logarithmic decrement with decrease in amplitude. Here, as in the period amplitude curves, we find that each successive curve lies above the next preceding one. These results would indicate that the greater twist of the wire through the large amplitudes increases the internal friction and that this increase in internal friction is not confined to the swings of larger amplitude but persists through the smaller amplitudes.

In the case of the logarithmic decrement-amplitude curves we again notice a striking difference from the corresponding curves for the platinum-iridium wires. In those wires, the logarithmic decrement at first, starting with the large amplitudes, increased slowly to a maximum value and then decreased very rapidly. It may be that here, too, the curve for the bismuth wire corresponds to that portion of the logarithmic decrement curve for the platinum-iridium wires where the amplitudes are small and the values of the decrement are decreasing.

Period and Vibration Number Curve.—For the last of the above four observations, that in which the initial amplitude was greatest, the periods were plotted as ordinates and the corresponding vibration numbers as abscissæ. For lack of space this curve is not shown here. It was found however that this curve also differs from the corresponding curve for the platinum-iridium wire.¹ In the latter case, the curve starts out almost parallel to the *x*-axis, then bends rapidly downward, and finally again approaches a horizontal direction. Neither in this, nor in any other curve of the same sort for the bismuth wire, could the tendency to start out in a direction parallel to the *x*-axis be detected. In other words, the curve is convex downward throughout its length. However, here again, it is

¹ Sieg, loc. cit., p. 425.

TABLE VII.

Exp. A.			Exp. B.		
No. of Swings.	Log. Dec.	Amp.	No. of Swings.	Log. Dec.	Amp.
8	.0125	30.8	8	.0148	70.9
10	.0123	26.5	10	.0147	60.6
20	.0121	23.2	10	.0142	51.3
20	.0119	20.1	10	.0137	43.7
20	.0118	17.6	10	.0134	37.4
20	.0114	15.3	10	.0132	32.1
20	.0112	13.5	20	.0128	27.6
40	.0110	11.9	20	.0126	23.9
40	.0107	9.2	20	.0121	20.7
40	.0103	7.3	20	.0118	18.0
40	.0102	5.7	20	.0115	13.9
40	.0100	4.6	20	.0112	10.6
			40	.0109	8.3
			40	.0106	5.1

Exp. C.			Exp. D.		
No. of Swings.	Log. Dec.	Amp.	No. of Swings.	Log. Dec.	Amp.
8	.0164	112.5	8	.0179	161.5
10	.0162	93.3	10	.0174	131.7
10	.0156	77.8	10	.0167	108.2
10	.0152	65.1	10	.0161	89.7
10	.0146	54.8	10	.0159	74.7
10	.0143	46.5	10	.0153	62.2
10	.0139	39.4	10	.0148	52.5
10	.0136	33.7	10	.0144	44.2
10	.0133	28.8	10	.0140	37.6
20	.0130	24.8	20	.0136	32.0
20	.0126	21.3	20	.0132	26.3
20	.0125	18.5	20	.0130	23.6
20	.0121	16.1	20	.0127	20.5
40	.0120	13.9	20	.0125	17.6
40	.0115	10.6	20	.0124	15.3
40	.0111	8.2	20	.0121	13.3
40	.0109	6.4	20	.0120	11.6
			20	.0116	10.1
			40	.0108	7.8
			40	.0106	5.6

that portion of the curve for the platinum-iridium wires that corresponds to the higher amplitudes that is missing in the curves for the bismuth wires.

In one other respect does the action of the bismuth wire differ from the platinum-iridium wire. In the case of the platinum-iridium wires, it was found that the wire made a larger number of vibrations in coming to rest when started with small amplitudes than when started with

larger amplitudes. Thus when the platinum-iridium wire was started with an initial amplitude of 364.3 degrees, it required 125 swings to fall to 5 degrees, while, when the wire was started with an initial amplitude of 14.3 degrees, 200 swings were required for the amplitude to fall to 6.15 degrees.¹ This same effect can be noted in the bismuth wire but not in anything like the same degree. In experiment *A* above, in which the initial amplitude was 34°.4, it required 80 vibrations for the amplitude to fall to 3.6 degrees. In experiment *D* in which the initial amplitude was 190.5 degrees, it required only 80 vibrations to cover the same interval.

V. EFFECT OF CHANGING THE MOMENT OF INERTIA.

The next experiment undertaken was to determine the effect of changing the moment of inertia of the vibrating system on the period-amplitude curve and on the logarithmic decrement curve. For this purpose, a wire .5 mm. in diameter and 95.7 cm. in length was used. Three experiments

TABLE VIII.

Diam. of wire, .5 mm. Length, 95.7 cm.

No. of Swing.	Exp. <i>A</i> . Mom. of Iner. 1.299 g. cm ² . Mass 150 g. Initial Amp. 89°.4. Temp. 26°.0.		Exp. <i>B</i> . Mom. of Iner. 1.382 g. cm ² . Mass 200 g. Initial Amp. 86°.5. Temp. 26°.0.		Exp. <i>C</i> . Mom. of Iner. 1.456 g. cm ² . Mass 200 g. Initial Amp. 82°.9. Temp. 25°.8.	
	Period.	Amplitude.	Period.	Amplitude.	Period.	Amplitude.
5	4.214	77.1	5.075	74.2	4.471	71.3
10	4.207	64.2	5.068	61.8	4.464	59.4
15	4.200	54.0	5.062	51.6	4.459	49.6
20	4.193	45.3	5.054	43.3	4.453	41.6
25	4.186	38.2	5.048	36.5	4.449	35.1
30	4.181	33.3	5.043	30.8	4.445	29.8
35	4.177	27.5	5.037	26.1	4.441	25.2
40	4.174	23.5	5.033	22.1	4.437	21.7
45	4.171	19.9	5.029	19.0	4.433	18.4
50	4.168	17.2	5.026	16.3	4.428	15.7
55	4.165	14.8	5.024	14.0	4.425	13.5
60	4.162	12.7	5.022	12.1	4.423	11.8
65	4.160	10.9	5.019	10.5	4.419	10.2
70	4.158	9.5	5.015	9.1	4.417	8.9
75	4.156	8.1	5.012	8.0	4.415	7.8
80	4.155	7.1	5.010	6.9	4.413	6.8
85	4.153	6.2	5.006	6.1	4.410	5.9
90	4.151	5.5	5.004	5.3	4.409	5.2
95	4.150	4.8	5.002	4.7	4.407	4.2
100	4.148	4.2	5.000	4.1	4.405	3.9
105	4.147	3.7	5.000	3.7		
110	4.147	3.2				

¹ Guthe and Sieg, loc. cit., p. 617.

were carried out, *A*, with a suspended weight having a mass of 150 g. and a moment of inertia of $1,299 \text{ g. cm}^2$; *B*, with a weight of 200 g. and a moment of inertia of $1,882 \text{ g. cm}^2$; and *C*, with a weight of 200 g. and a moment of inertia of $1,456 \text{ g. cm}^2$. By comparing experiments *A* and *B*, it was possible to determine the effect of a change in both the moment of inertia and the mass of the suspended weight. By comparing *B* and *C*, it was possible to determine the effect of changing the moment of inertia only. The results are shown in Table VIII.

The period-amplitude curves are of the same general appearance as those found in the experiments described above. In these experiments, it was found necessary to use smaller amplitudes since the wire had a lower elastic limit than the one of smaller cross-sectional area used in the earlier experiments.

TABLE IX.

B factor = .8813.*A* factor = 1.0615.

Old Period.	New Period.	Amplitude.	Old Period.	New Period.	Amplitude.
5.975	4.473	74.2	4.214	4.473	77.1
5.068	4.466	61.8	4.207	4.465	64.2
5.062	4.461	51.6	4.200	4.458	54.0
5.054	4.454	43.3	4.193	4.451	45.3
5.048	4.449	36.5	4.186	4.443	38.1
5.043	4.444	30.8	4.181	4.438	33.4
5.037	4.439	26.1	4.177	4.434	27.5
5.033	4.436	22.1	4.174	4.430	23.5
5.029	4.432	19.0	4.171	4.427	19.9
5.026	4.429	16.3	4.168	4.424	17.1
5.024	4.428	14.0	4.165	4.421	14.8
5.022	4.426	12.2	4.162	4.418	12.7
5.019	4.423	10.3	4.160	4.416	10.9
5.015	4.420	9.1	4.158	4.413	9.5
5.012	4.417	8.0	4.156	4.411	8.1
5.010	4.415	6.9	4.155	4.410	7.1
5.006	4.412	6.1	4.153	4.408	6.2
5.004	4.410	5.3	4.151	4.406	5.5
5.002	4.408	4.7	4.150	4.405	4.8
5.000	4.407	4.2	4.148	4.404	4.2
5.000	4.407	3.7	4.147	4.402	3.7
			4.147	4.402	3.2

In order to afford a means of comparison for the three curves, the three series of observations were all reduced to the same period, that of experiment *C*. To do this, the three curves were produced until they cut the *y*-axis and from these points of intersection, a reduction factor was obtained. All the values for the periods of the curve to be reduced were then multiplied by this factor. This operation will have the effect of making the two curves to be compared start with the same period at

zero amplitude. In Table IX, are shown the results for experiments *A* and *B* reduced in the manner described above so as to correspond to that of *C*.

These reduced values were plotted and the curves are shown in Fig. 7. Curve *A* represents the results for experiment *A* and curve *C* the results for experiments *B* and *C*. It is found from Fig. 7, that the curve for

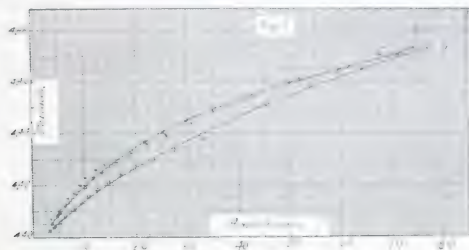


Fig. 7.

experiment *A* starts and finishes at about the same places as that for experiment *C*, but the middle portion lies quite a little below that for *C*. In other words, the curve for *A* is much flatter than that for *C*. On the other hand, the curves for *B* and *C* very nearly coincide. In fact, the variation in position of the two sets of points in the combined curve is no greater than the variation in the position of the points in either curve considered alone. When we remember that in observations *A* and *C*, both the mass of the vibrating system and its moment of inertia were varied, while in *B* and *C* only the moment of inertia was varied, we must conclude that, if we keep the stress to which the wire is subjected constant, the period will be the same function of the amplitude no matter what the moment of inertia, while if the stress as well as the moment of inertia is varied, the period will be a different function of the amplitude.

From the formula for the period, $T = 2\pi \sqrt{I/T}$, we should expect the reduction factor in each case to be equal to the square root of the ratio of the corresponding moments of inertia. The reduction factor for reducing observation *A* to observation *C* is 1.061. The value of $\sqrt{I_A/I_C}$ is 1.059. The reduction factor for reducing *C* to *B* is .881 while the value of $\sqrt{I_B/I_C} = .879$. When we remember that the factors here given were obtained from the curves, the agreement is remarkably close.

For lack of space the curves showing the relation between the logarithmic decrements and amplitudes in this experiment are not shown but it was found that here again we have a very good agreement between the curves for experiments *B* and *C* while the curve for experiment *A* differs to quite a marked extent from the other two, the curve for experiment *A*

lying below that for experiments *B* and *C*. This difference is especially noticeable in that portion of the curve corresponding to the larger amplitudes. This indicates that the shape of the logarithmic decrement-amplitude curve is also independent of the moment of inertia of the suspended weight but does depend upon the stress to which the wire is subjected. The effect of increasing the mass of the vibrating system is to increase the values for the logarithmic decrement especially for the higher amplitudes.

VI. THE EFFECT OF VARIATION IN THE LENGTH OF THE WIRE.

For determining the effect of a variation in the length of the wire upon the period-amplitude curve, a wire .25 mm. in diameter was used. Observations were taken using three different lengths: the first 104.8 cm., the second 82.0 cm. and the third 62.6 cm.

In all three cases, a cylinder weighing 50 g. and having a moment of inertia of 133 g. cm². was used. The results obtained are given in Table X.

TABLE X.

Diam., .25 mm. Moment of inertia, 133 g. cm².

No. of Swing.	Exp. A. Length 104.8 cm. Initial Amp. 175°.4. Temp. 26°.0.		Exp. B. Length 82.0 cm. Initial Amp. 136°.9. Temp. 26°.5.		Exp. C. Length 62.6 cm. Initial Amp. 105°.3. Temp. 27°.0.	
	Period.	Amplitude.	Period.	Amplitude.	Period.	Amplitude.
5	5.306	149.1	4.734	116.1	4.131	88.8
10	5.296	121.5	4.725	94.5	4.126	72.3
15	5.290	100.0	4.717	77.2	4.120	59.6
20	5.283	82.6	4.710	63.7	4.115	49.2
25	5.277	68.7	4.704	52.7	4.109	40.8
30	5.271	57.2	4.699	43.9	4.104	34.1
35	5.265	47.9	4.695	36.6	4.100	28.5
40	5.260	40.3	4.690	30.7	4.097	24.0
45	5.256	33.9	4.686	25.8	4.094	20.2
50	5.252	28.9	4.682	21.9	4.091	17.3
55	5.248	24.5	4.679	18.5	4.089	14.7
60	5.245	21.0	4.675	15.8	4.085	12.6
65	5.242	17.8	4.673	13.6	4.082	10.8
70	5.239	15.4	4.670	11.6	4.080	9.2
75	5.237	13.3	4.668	9.9	4.078	8.1
80	5.235	11.5	4.667	8.6	4.076	7.0
85	5.233	9.9	4.666	7.4	4.075	6.1
90	5.232	8.6	4.664	6.5	4.073	5.3
95	5.231	7.5	4.663	5.6	4.072	4.5
100	5.230	6.5	4.662	4.9	4.070	4.0
105	5.230	5.6	4.661	4.3	4.069	3.5
110	5.229	5.0			4.068	3.1
115	5.228	4.4			4.067	2.7
120	5.227	3.8				

In this case, as in the determination of the effect of a change in moment of inertia, it is necessary to reduce all experiments to the same period in order to obtain a basis for comparison. Experiment *B* was chosen as the basis for the comparison and the periods in the other two series reduced to this. The factors for reduction were obtained in the same way as before, that is, by determining the points of intersection of the curves with the *y*-axis. In this way, the curves will all start with the same period at zero amplitude. The reduced values for experiments *A* and *C* are given in Table XI.

TABLE XI.

A factor = .8912.*C* factor = 1.1458.

Old Period.	New Period.	Amplitude.	Old Period.	New Period.	Amplitude.
5.306	4.729	149.1	4.131	4.733	88.8
5.296	4.720	121.5	4.126	4.727	72.5
5.290	4.715	100.0	4.120	4.720	59.6
5.283	4.708	82.6	4.115	4.715	49.2
5.277	4.703	68.7	4.109	4.708	40.8
5.271	4.698	57.2	4.104	4.702	34.1
5.265	4.692	47.9	4.100	4.698	28.5
5.260	4.688	40.3	4.097	4.694	24.0
5.256	4.684	33.9	4.094	4.691	20.2
5.252	4.680	28.9	4.091	4.687	17.3
5.248	4.677	24.5	4.089	4.684	14.7
5.245	4.674	21.0	4.085	4.680	12.6
5.242	4.672	17.8	4.082	4.677	10.8
5.239	4.669	15.4	4.080	4.675	9.2
5.237	4.667	13.3	4.078	4.672	8.1
5.235	4.665	11.5	4.076	4.670	7.0
5.233	4.664	9.9	4.075	4.669	6.1
5.232	4.663	8.6	4.073	4.667	5.3
5.231	4.662	7.5	4.072	4.665	4.5
5.230	4.661	6.5	4.070	4.663	4.0
5.230	4.661	5.6	4.069	4.662	3.5
5.229	4.660	5.0	4.068	4.661	3.1
5.228	4.659	4.4	4.067	4.660	2.7
5.227	4.658	3.8			

In reducing the results of experiments *A* and *C* to compare with those of *B*, we should expect the factor in each case to be equal to the ratio of the square roots of the lengths, since the period of vibration varies as the square root of the length. The factor for the reduction of the data of experiment *A* to those of experiment *B* is .8912. The value $\sqrt{L_B/L_A}$ is .8846, giving a difference of .0066. The factor for the reduction of *C* to *B* is 1.1458. The value of $\sqrt{L_B/L_C}$ is 1.1445, giving a difference of .0013.

For lack of space the curves for these results are not shown but it was found that the curves did not coincide in this case as they did in the moment of inertia experiment. The curves for the shorter lengths were found to be much steeper than for the longer length. The amounts of decrease in period were about the same in all three cases. It must be remembered, however, that in this experiment we are not comparing corresponding points in the wire. That is to say, the point whose arc of vibration we are measuring in experiment *C* would vibrate through a much larger arc for the same amount of twist in the wire, if the point were at the end of a longer wire such as we have in experiment *A*. For this reason, a reduction factor must be applied to the amplitudes as well as to the period. These reduction factors were obtained by comparing the amplitudes corresponding to the same period in the two curves under consideration. All the amplitudes in the given experiment were then multiplied by this reduction factor. In this reduction, experiment *B* was taken as the standard and the amplitudes of *A* and *C* reduced so as to correspond. The reduced results for experiments *A* and *C* are shown in Table XII.

TABLE XII.

Experiment *A*. Factor = .732.Experiment *C*. Factor = —.

Old Amp.	New Amp.	Period.	Old. Amp.	New Amp.	Period.
149.1	110.1	4.729	88.8	128.7	4.733
121.5	88.9	4.720	72.5	105.1	4.727
100.0	73.2	4.715	59.6	86.4	4.720
82.6	60.5	4.708	49.2	71.1	4.715
68.7	50.3	4.703	40.8	59.2	4.708
57.2	42.4	4.698	34.1	49.4	4.702
47.9	35.1	4.692	28.5	41.3	4.698
40.3	29.5	4.688	24.0	34.8	4.694
33.9	24.8	4.684	20.2	29.3	4.691
28.9	21.1	4.680	17.3	25.0	4.687
24.5	17.9	4.677	14.7	21.3	4.684
21.0	15.4	4.674	12.6	18.3	4.680
17.8	13.0	4.672	10.8	15.7	4.677
15.4	11.3	4.669	9.2	13.3	4.675
13.3	9.6	4.667	8.1	11.7	4.672
11.5	8.1	4.665	7.0	10.2	4.670
9.9	7.2	4.664	6.1	8.8	4.669
8.6	6.3	4.663	5.3	7.7	4.667
7.5	5.5	4.662	4.5	6.5	4.665
6.5	4.7	4.661	4.0	5.8	4.663
5.6	4.1	4.661	3.5	5.1	4.662
5.0	3.7	4.660	3.1	4.5	4.661
4.4	3.2	4.659	2.7	3.9	4.660
3.8	2.8	4.658			

The curves obtained from these results together with the original curve for experiment *B* are shown in Fig. 8. We see from that figure that we have a remarkably close agreement between the three sets of points.



Fig. 8.

If the curves for these experiments were straight lines, we would expect the reduction factors for the amplitudes to be equal to the ratio of the lengths. As it is they are quite different. The reduction factor for changing *A* to *B* is .732 while the ratio of the lengths is .782. The reduction factor for the amplitudes of *C* is 1.450, while the ratio of the lengths is 1.310.

We must conclude from the fact that by merely applying constant factors to the two variables in these observations, the three curves can be made to coincide, that the period in each case is the same function of the amplitude. It also indicates that the wire is uniform throughout its length and that its peculiar behavior is not due to any particular portion of the wire.

VII. THE EFFECT OF VARIATION IN DIAMETER ON THE PERIOD-AMPLITUDE CURVE AND THE LOGARITHMIC DECREMENT-AMPLITUDE CURVE.

To determine the effect of varying the diameter of the wires upon the period-amplitude curve and the logarithmic decrement-amplitude curve, two wires of different diameter were used with suspended weights of such a mass that the stress to which the wire was subjected was the same in both cases.

In this experiment, the wires were of .25 mm. and .5 mm. in diameter respectively. Since the cross-sectional area of the first was one fourth that of the second, the mass of the suspended weight in the first case was one fourth that in the second. Masses of 50 g. and 200 g. respectively were used.

TABLE XIII.

No. of Swing.	Exp. A. Diam. .25 mm. Length 97.9 cm. Mass 50 g. Moment of Inertia 133 g. cm ² . Temp. 28°.1.		Exp. C. Diam. .5 mm. Length 97.9 cm. Mass 200 g. Moment of Inertia 1,456 g. cm ² . Temp. 26°.0.	
	Period.	Amplitude.	Period.	Amplitude.
5	5.320	142.4	4.521	72.9
10	5.309	114.7	4.514	60.7
15	5.299	92.7	4.509	50.7
20	5.292	75.6	4.503	42.8
25	5.285	62.1	4.499	35.9
30	5.279	51.2	4.496	30.5
35	5.274	42.4	4.491	25.8
40	5.268	35.3	4.487	22.2
45	5.263	29.6	4.483	18.8
50	5.259	24.9	4.478	16.1
55	5.256	21.2	4.475	13.8
60	5.253	17.9	4.472	12.1
65	5.251	15.4	4.468	10.4
70	5.249	13.1	4.466	9.1
75	5.246	11.3	4.464	8.0
80	5.243	9.3	4.462	7.0
85	5.241	8.4	4.459	6.0
90	5.239	7.2	4.458	5.3
95	5.238	6.2	4.457	4.6
100	5.237	5.4	4.456	4.0
105	5.236	4.8		
110	5.235	4.1		
115	5.235	3.6		
120	5.234	3.2		

In this experiment, it was necessary to use a smaller initial amplitude for the wire of large diameter than for the one of small diameter because of the lower elastic limit in the one case than in the other. Of course,

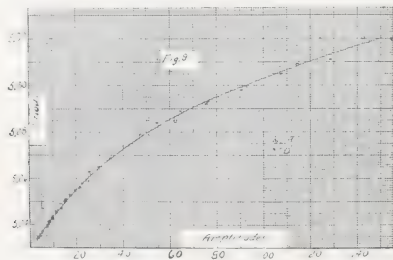


Fig. 9.

here again, we must apply a reduction factor to the periods in order to afford a basis of comparison. This was done, the factor being obtained

in the same way as before. Experiment *A* was taken as the standard and *B* reduced to correspond.

The factor for reducing the period should theoretically be equal to the inverse ratio of the squares of the diameters multiplied by the ratio of the square-roots of the moments of inertia. This operation gives a factor of 1.208, while that found from a comparison of the curves was 1.176.

If a second reduction factor be applied to the amplitudes it is found that the curves coincide. These reduced results are shown in Table XIV. and the two sets of points are plotted in Fig. 9.

TABLE XIV.

Factor = 2.12.

Old Amp.	New Amp.	Period.	Old Amp.	New Amp.	Period.
72.9	154.5	5.320	13.8	29.2	5.265
60.7	128.7	5.311	12.1	25.7	5.263
50.7	107.5	5.305	10.4	22.5	5.258
42.8	90.7	5.298	9.1	19.3	5.255
35.9	76.1	5.293	8.0	17.0	5.253
30.5	64.7	5.289	7.0	14.9	5.250
25.8	54.7	5.284	6.0	13.2	5.247
22.2	47.1	5.279	5.3	11.2	5.245
18.8	39.9	5.274	4.6	9.8	5.243
16.1	34.1	5.269	4.0	8.0	5.241

From the fact that the curves for the two observations can be made to coincide by applying constants to the two variables, we must conclude that when the stress to which the wire is subjected is kept constant, the period is the same general function of the amplitudes no matter what the diameter of the wire.



FIG. 10.

The Logarithmic Decrement-Amplitude Curve.—The logarithmic decrements in these two experiments were computed and plotted against the corresponding values of the amplitudes. The results of these computations are shown in Table XV. and the curves in Fig. 10.

TABLE XV.

Exp. A.			Exp. B.		
No. of Swings.	Log. Dec.	Amplitude.	No. of Swings.	Log. Dec.	Amplitude.
8	.0191	142.2	8	.0161	71.3
10	.0186	114.7	10	.0158	59.4
10	.0181	92.7	10	.0153	49.6
10	.0174	75.6	10	.0150	41.8
10	.0169	62.1	10	.0147	35.1
10	.0166	51.2	20	.0143	29.8
10	.0161	42.4	20	.0141	25.2
10	.0156	35.3	20	.0139	21.7
10	.0152	29.6	20	.0136	18.4
20	.0147	24.9	20	.0133	15.7
20	.0142	21.2	20	.0128	13.5
20	.0140	17.9	40	.0126	11.8
20	.0137	15.4	40	.0120	8.9
20	.0133	13.1	40	.0118	6.8
20	.0130	9.7			
20	.0127	7.2			
20	.0122	5.4			
20	.0117	4.1			

It will be noticed from Fig. 10 that while the logarithmic decrement curves start from about the same point, the one for the small diameter is steeper than that for the wire of larger diameter.

SUMMARY.

1. The elastic properties of bismuth wires have been investigated and it has been found that they display some of the same peculiar properties shown by the platinum-iridium wires investigated by Guthe and Sieg. When the wires were vibrated torsionally, the period of vibration and the logarithmic decrement were found to decrease enormously with the decrease in amplitude. The curves for the bismuth wires representing the relations between (*a*) the period and amplitude, (*b*) the logarithmic decrement and amplitude, and (*c*) the period and vibration number, were found to be lacking in certain characteristics found in the corresponding curves for the platinum-iridium wires. These characteristics were for the most part, however, found at amplitudes for the platinum-iridium wires that could not be reached with the bismuth wires, because of the low elastic limit of the latter.

2. It was found that, in two experiments in which the mass of the vibrating system was kept constant but the moment of inertia varied, the period-amplitude curves in the two cases could be made to coincide by applying a reduction factor to the periods in one set of observations.

This reduction factor was found to be equal to the ratio of the square roots of the moments of inertia used in the two experiments. This indicates that the mathematical relation between the period and amplitude does not depend upon the rapidity of motion of the vibrating system. The logarithmic decrement-amplitude curves in the two cases were found to coincide.

If the load as well as the moment of inertia was varied, it was found that when the proper reduction factor was applied to the periods, the two curves did not coincide, the curve corresponding to the vibrating system having the smaller mass being flatter than the other. The curves for the logarithmic decrement did not coincide, the greater values for the logarithmic decrement being found in the case in which the mass of the suspended weight was greatest.

3. When the length of the wire was varied, it was found that by applying reduction factors to the periods and amplitudes, the period-amplitude curves for the different experiments could be made to coincide, indicating that the period is the same general function of the amplitude in all cases. This also indicates that the wire is uniform throughout its length and that its peculiar behavior is not due to any particular section of the wire.

4. Two wires of different diameter were used with suspended weights of such a mass that the stresses to which the wires were subjected were the same in each case. In this experiment, also, by applying the proper factors to the amplitudes and periods the curves could be made to coincide. The logarithmic decrement curve for the smaller wire was found to lie above that for the wire of larger diameter, indicating a greater damping effect in the former.

In conclusion, the writer wishes to express his appreciation of the helpful advice and kindly interest of Prof. K. E. Guthe, at whose suggestion this investigation was undertaken.

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NOTES ON OPTICAL CONSTANTS OF METALS

By J. T. LITTLETON, JR.

INTRODUCTION.

THIS work consists in the determination of the values of the optical constants, that is, n the refractive index and k the absorptive index, for silicon and ductile tungsten, and a study of the effect of heat treatments on different steels. Observations have been made on silicon and tungsten by von Wartenberg¹ and on silicon by Ingersoll and Littleton.² The specimens used in this investigation are much purer than the one used by von Wartenberg, and, in addition to observations (by another method), on the same piece studied by Ingersoll and Littleton measurements are made on a piece with a different crystalline structure, and on one showing the Hall and thermo-electric effects in a direction different from the others. The metallic tungsten used in this work is of an entirely different form from the one used by von Wartenberg.

Many observers have measured the optical constants of steel, but with no concordance of results. This lack of agreement among different experimenters must be largely due to the fact that measurements were made on specimens of entirely different carbon content and having no similarity as regards heat treatment.

Hagen and Rubens³ give the values of 55.4 per cent. for the reflecting power of soft steel and of 60.0 per cent. for hard steel for light of a wavelength of $6,000\mu$ and Drude⁴ using sodium light gives for steel the value 58.5 per cent., but in neither case is the carbon content specified or is the heat treatment prescribed other than merely by the words hard and soft. But it is well known that these two factors have a great influence on all of the physical properties of the metal. It is therefore of interest to see whether the optical properties are so affected, and whether by this means the apparent disagreement between different experimenters can be explained.

EXPERIMENTAL METHOD.

Since the method used for the determination of the values of n and k is that used by Drude,⁵ no experimental details need be given.

¹ D. Phys. Gesell. Verh., 12, p. 105, 1910.

² Phys. Rev., 31, Nov., 1910.

³ Zeits. f. Instrumentk., 22, 52, 1902.

⁴ Ann. Phys., 39, 481, 1890.

⁵ Ann. Phys., 39, 481, 1890.

All grinding was done with graded carborundum, and the polishing with rouge on a pitch tool or with rouge on broad-cloth. But since this latter method has a tendency to give a relief polish it is not desirable in all cases.

As a source of light fused sodium chloride in a blast lamp was used for the measurements on silicon and tungsten, but the Meker burner with a platinum holder for the sodium chloride used for the steels proved much more satisfactory.

Observations were made at principal incidence and principal azimuth, that is, at that angle of incidence, at which light plane polarized at an angle of 45° with the plane of incidence, becomes circularly polarized after reflection from the metallic surface. Angles of incidence could be read to $30''$ and azimuth to 0.1° .

If ϕ be the angle of principal incidence and $\bar{\psi}$ the principal azimuth the well-known Drude formulæ become for this position:

$$n = \sin \phi \tan \bar{\phi} \cos 2\psi + \frac{\cos \bar{\phi} \cos 2\bar{\psi}}{2},$$

$$k = \tan 2\psi(1 - \cot^2 \phi).$$

The reflecting power is calculated from n and k by:

$$R = \frac{n^2(1 + k^2) + 1 - 2n}{n^2(1 + k^2) + 1 + 2n}$$

I. SILICON.

Observations were taken on four pieces of silicon obtained from the Carborundum Co., of Rochester, N. Y., having a purity of 99.75 per cent. No. 1 had a good black polish, though not free from scratches, No. 2 was from the same plate as No. 1, and was scratched in only one direction with carborundum which had remained suspended in water for five minutes, No. 3 was the flat surface of a crystal and No. 4 was a piece giving thermoelectric effects and Hall effects in a direction opposite to the others. Since these give the same values for n and k to within the possible experimental error, results will be given for the first piece only, this having the best polish of the four. This is also the same plate on which measurements out in the infra-red to 2.5μ were made by Ingersoll,¹ and by Ingersoll and Littleton² by another method.

The means of ten observations at angles of incidence equal to 68° , 70° , 72° , 74° , and 76° give:

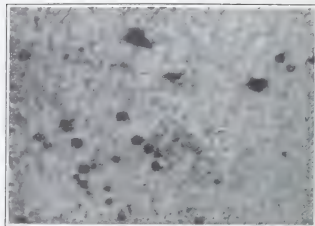
¹ Astr. Phy. Jour., Vol. XXXII., p. 265, 1910.

² Phys. Rev., Vol. XXXI., p. 489, 1910.





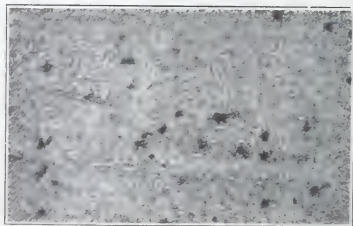
No. 1D.
High power.



No. 1D.
Low power.



No. 5D.
High power.



No. 5D.
Low power.

$n = 4.24$, $k = 0.118$, $\phi = 76^\circ 45'$, $2\psi = 6^\circ 52'$, $R = 37.8$ per cent.

The greatest deviation from the mean was 1.5 per cent. for n and 7 per cent. for k , ϕ and 2ψ were calculated and the above value of R is the calculated reflecting power. R measured by a Martens-Koenig spectrophotometer is 37.7 per cent. This result is accurate to 0.5 per cent. The reflecting power for the Reststrahlen from quartz of 9 μ wavelength was measured by means of a Rubens thermopile and was found to be 33.5 per cent.

Von Wartenberg using silicon 95 per cent. pure and light of a wavelength 5.790 μ gets:

$n = 3.87$, $k = 0.116$, $\phi = 75^\circ 38'$, $2\psi = 7^\circ 3'$, $R = 35.7$ per cent.

This difference between the two determinations is readily explained by the difference in purity.

II. TUNGSTEN.

A thin plate of ductile tungsten having the dimensions 1.5 by 0.5 square centimeters was obtained from the General Electric Co. Scratches did not have much effect on either principal incidence or principal azimuth, but the final observations were on a surface practically free from scratches.

The means of ten sets of measurements of ϕ and 2ψ gave:

$n = 3.46$, $k = 0.94$, $\phi = 78^\circ 34'$, $2\psi = 44^\circ 3'$, $R = 54.5$ per cent.

Von Wartenberg using a form of pressed tungsten and light of a wavelength equal to 5.790 μ gets the following results:

$n = 2.76$, $K = 0.98$, $\phi = 76^\circ 0'$, $2\psi = 46^\circ 20'$, $R = 48.6$ per cent.

This difference is no doubt due to the different form of metal used.

III. THE EFFECT OF HEAT TREATMENTS AND CARBON CONTENT ON THE OPTICAL PROPERTIES OF STEEL.

Measurements were made on five surfaces of 0.44 per cent. carbon steel, on five of 1.28 per cent. carbon steel, on one of about 3.5 per cent. carbon and one of pure iron. These steels were obtained from Prof. E. D. Campbell of the department of chemistry and are of accurately known composition and heat treatment.

Steels may be divided into four classes, the basis of division being the crystalline structure as controlled by heat treatments. CLASS I. is a mixture of the segregated particles of the carbides of iron in a matrix of pure iron, and is obtained by holding the metal at a temperature of about 600° C. for twenty-four hours or longer, which treatment allows the carbides of iron to collect into large particles. CLASS II. is very similar, differing only in degree, the particles of the iron carbides being very small.

This structure is obtained by slow annealing from about 900° C. or by quenching from 900° C. and reheating to about 600° C. and holding at this temperature for eight or ten hours. The carbides begin to go out of solution and to collect into very fine particles. This form of steel is called perlite. CLASS III. is, according to Campbell,¹ a supersaturated solution of the carbides of iron in α iron. This structure is obtained by quenching from about 900° C. and reheating to about 340° C. and holding at this temperature for ten or more hours. This structure is called troostitic. In opposition to Campbell's view is the theory that this steel consists of very finely divided particles of the carbides of iron mechanically mixed in the iron crystal. CLASS IV. is the quenched or hardened steel and is obtained by holding the specimen at a temperature around 900° C. for thirty minutes and quenching in ice water. This gives a solid solution of the carbides of iron in small γ iron crystals.

These treatments cause quite a difference between the two extremes of structure, that is, between the segregated iron and the quenched and hardened. The micro-photographs of the 1.28 per cent. carbon steel show this characteristic difference. In the segregated iron the segregated particles are clearly shown under the low power magnification and one large particle is shown under the high power. The difference between the two structures is clearly visible. Microscopic examination of the surfaces prepared from the other specimens showed them to be good examples of their class.

After microscopic examination the etching was ground off and the surface repolished and the observations taken. The means of ten observations on these surfaces are given in the following table.

Optical Constants of Steel.

No.	Per Cent. C.	Φ	2ψ	n	k	R
No. 1C	0.44	77° 10'	53° 55'	2.59	1.30	57.2
No. 2C	0.44	77° 11'	53° 55'	2.59	1.30	57.2
No. 3C	0.44	77° 18'	53° 55'	2.61	1.30	57.5
No. 4C	0.44	77° 16'	53° 55'	2.61	1.30	57.5
No. 5C	0.44	77° 18'	53° 55'	2.61	1.30	57.5
No. 1D	1.28	77° 16'	53° 30'	2.63	1.28	57.4
No. 2D	1.28	77° 26'	53° 30'	2.67	1.28	57.4
No. 3D	1.28	77° 12'	53° 30'	2.63	1.28	57.6
No. 4D	1.28	77° 30'	53° 30'	2.68	1.28	57.5
No. 5D	1.28	77° 28'	53° 30'	2.68	1.28	57.5
No. 1E	3.5	77° 35'	52° 24'	2.77	1.23	57.0
No. 1F	0.00	77° 1'	54° 10'	2.53	1.31	56.2
Drude	Steel	77° 8'	55° 38'	2.41	1.41	58.5
Drude	Iron	76° 30'	54° 58'	2.36	1.36	56.2

¹ Jour. of Iron and Steel Inst., p. 318, 1908.

Assuming a correct polish these results are correct to the second decimal figure.

No. 1C was annealed for sixteen hours from 900° C. and is a segregated piece. No. 2C was quenched from 900° C., reheated to 600° C. and held at this temperature for twelve hours. No. 3C was quenched from 900° C. and reheated to 340° C. and held at this point for twelve hours. No 4C was quenched from 900° C., reheated to 200° C. and held at this temperature for eighteen hours. This reheating does not affect the structure to a noticeable degree, yet it softens the steel sufficiently to allow cutting. No. 5C was held at 1000° C. for thirty minutes and then quenched. No. 1D was held at 600° C. for twenty-four hours. No. 2D was quenched and reannealed, the exact time and temperatures not being known. Microscopic examination showed that it belonged more to class III. than to class II. No. 3D was cooled from 1000° C. to 200° C. during sixteen hours. This is a good specimen of perlite. No. 4D was quenched from 900° C. and heated to 340° C. No. 5D was held at 950° C. for thirty minutes and quenched in ice water.

Nos. 1C and 1D belong to class I. Nos. 2C and 3D to class II., Nos. 3C, 2D and 4D to class III., Nos. 4C, 5C and 5D to class IV.

Drude's¹ results are given for comparison.

DISCUSSION OF RESULTS.

It is seen that the results of Drude differ from those given here and that the difference is much larger than the error of observation. The difference lies mainly in the values obtained for principal azimuth, and this value is affected by scratches and not so much by the purity of the surface. Impurity of the surface, that is, a surface film, tends to decrease the value of principal incidence, and these results do not indicate any such impurity, the principal incidence in all cases being larger than that of Drude. From previous work² by the author on the optical constants of iron and nickel alloys the curve plotted between n and the per cent. of iron intersects the iron axis at a value of n equal to 2.48, and the curve between k and the per cent. of iron could be drawn to the iron axis at a point giving the value for k of 1.31. This leads to the conclusion that the iron observed by Drude contained some other metal, or else that there is some constant error in the method of polishing used here. But if for any reason these values of n are too high and of k too low they are consistently so, and the difference between the different steels exists independent of the absolute values of the optical constants.

¹ Ann. der Phys., 39, 481, 1890.

² Phys. Rev., 33, p. 453, 1911.

The fact that classes I. and II. give the same values for n and k proves that the light reflected from the large particles of the carbides of iron combines with that from the pure iron and gives light of the same form as is obtained from the small particles and the pure iron. Since this proves that the size of the particles up to this extent has no effect and since classes III. and IV. have the same values for n (and this value is different from that of classes I. and II.) the conclusion is that the carbides of iron have some effect on the iron molecule in both the hard steel and the troostitic form. This furnishes good evidence in support of the theory held by Campbell mentioned previously.

The decrease in k caused by an addition of carbon is so small that a change caused by heat treatment cannot be observed. But the changes in n caused by changes in carbon content and by heat treatments are quite large. Hence lack of similarity in these two factors could easily account for any lack of agreement between measurements of the optical constants of steels of unknown compositions and heat treatments.

In conclusion the author wishes to express his thanks to Prof. C. E. Mendenhall, of the University of Wisconsin, for assistance in the first part of this work, to Prof. E. D. Campbell, of the department of chemistry of this university, for suggestions and for specimens used in the work on steel, to Mr. A. E. White for assistance on the micro-photographs, and to Prof. K. E. Guthe for the apparatus used and for his interest in the progress of the work.

PHYSICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June, 1912.



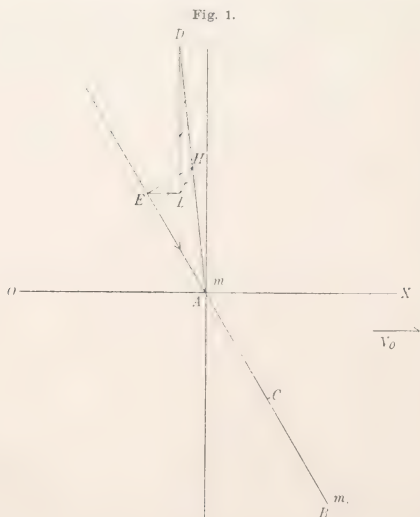


On Coulomb's Laws of Friction.

By PETER FIELD.

Coulomb's laws of friction¹⁾ state that when one body slides over another the frictional force is

- 1) proportional to the normal pressure,
- 2) independent of the magnitude of the areas which are in contact,
- 3) independent of the relative velocities of the two bodies.



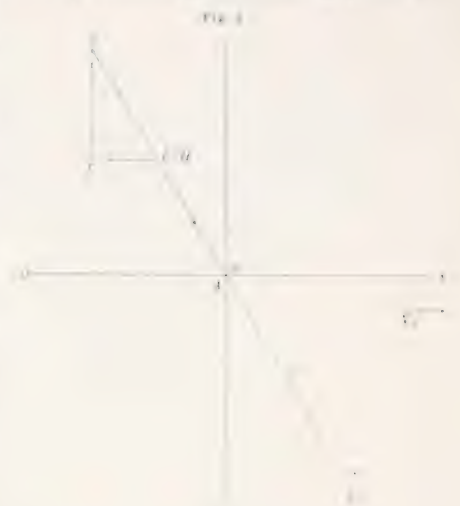
In his *Leçons sur Le Frottement*, published in 1895, Painlevé discussed a number of interesting friction problems under the assumption that the frictional force obeys these laws. The particularly interesting thing brought out in Painlevé's discussion is the fact, that while the normal reaction is independent of the coefficient of friction in some problems, in general this is not the case. The discussion

1) Coulomb, *Théorie des machines simples, mémoires des Savants étrangers*, tome X, 1781.

of the last class of problems brings to light a difficulty the nature of which is most easily understood by considering the following problem, first treated by Painlevé in his *Leçons*¹⁾ and later by others.²⁾

Given two particles m, m_1 (Fig. 1) each of unit mass which are connected by a weightless rod AB : m is constrained to move along a rough horizontal tube OX and the particles are to remain in the given vertical plane. Determine the initial values of the acceleration of m and of the centroid C for different values of the coefficient of friction, μ .

For a small value of μ the problem presents no difficulties, but if μ is sufficiently large the equations of motion either can not be satisfied at all or they permit two different solutions. In the one case it is not possible to satisfy the equations of motion no matter whether the normal component of the reaction of the tube is chosen upward or downward, while in the second case it may be chosen either way. The



1) Also in *Comptes rendus*, t. CXXI, 1895, p. 112.

2) Appell, *Mécanique* Vol. II, p. 133, 3^d edition.

and the motion is a translation at the given moment, the projection of the accelerations of m , C , m_1 , along the line AB have a common value j_r . From the motion of the centroid it follows that the sum of the projections of R and $2mg$ along AB is equal to $2mj_r$ or the sum of the projections of $\frac{1}{2}R$ and mg is equal to mj_r .

The forces which act on the particle at A are mg , R and T . Now we know that the sum of their projections along AB is mj_r and we also know that the sum of the projections of mg and $\frac{1}{2}R$ along the rod is mj_r ; therefore the sum of the projections of $\frac{1}{2}R$ and T along the rod is zero. Figure 1 can therefore be constructed by assuming an arbitrary length AD for R (and for the present the normal component of the reaction of the tube will be assumed upward): the projection of $\frac{1}{2}R$ in the direction of AB gives the stress in the rod. As the particle at A has no acceleration along the vertical, the sum of the vertical projections of R , T , and mg is zero; this enables us to construct $mg = DL$. Calling the accelerations of the particle at A and of the centroid j_a and j_c respectively, it follows that the sum of the horizontal components of R and T is $mj_a = EL$ and the sum of $\frac{1}{2}R$ and mg is $mj_c = HL$. Figure 1 exhibits

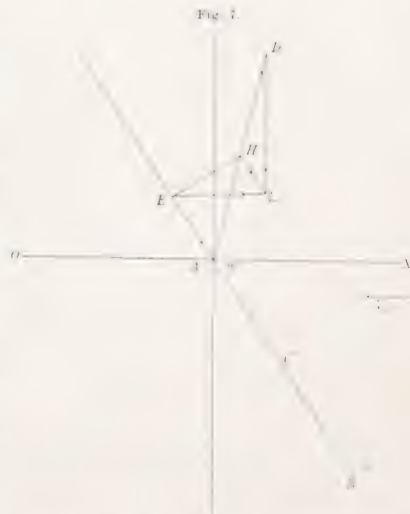


Fig. 8.

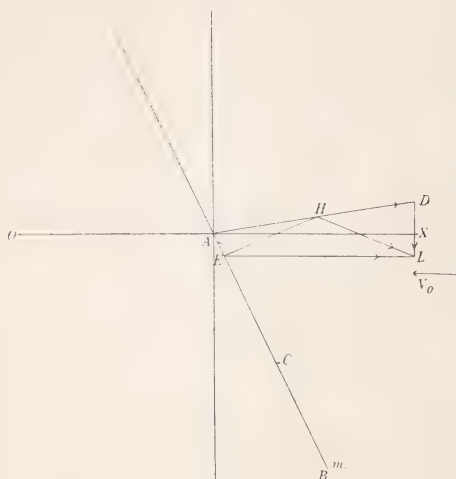
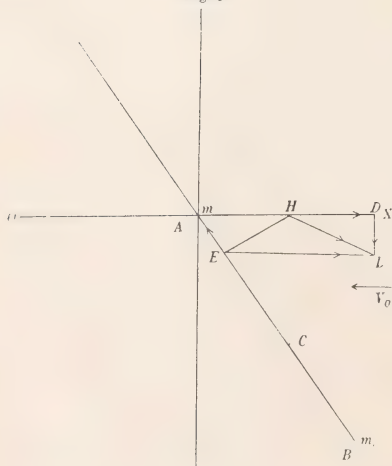


Fig. 9.



the magnitudes of the different quantities in which we are interested. The second figure differs from the first only in that the friction angle has been increased so that the direction of R and T is the same. In the third figure mg is small, while in the fourth it is zero in comparison with the other quantities.

In case 4 m is instantaneously brought to rest and the motion becomes a rotation about A as a fixed point. It is interesting to notice that if instead of thinking of EL as representing

$m j_a$ we think of it as representing $m j_a dt = -m V_0$, then HE represents $HL + LE = m j_c dt + m V_0 = m V_c$, where V_c is the velocity of the centroid after the particle at A is stopped and this velocity is at right angles to the rod as it should be.

A still larger value of the coefficient of friction would give the same solution as 4, as only enough friction would come into play to prevent any motion at A . If however we supposed A to move in such a case, we would be lead to the conclusion that mg must be directed up-

ward as in Fig. 5. Fig. 6 is inserted to show that if the normal component of the reaction of the tube is assumed downward, the same difficulty is encountered.

in 11 we have a finite value of the coefficient of friction and infinite values of the accelerations just as in Fig. 4. Presumably the proper interpretation of 11 is that A is instantaneously brought to rest and the normal component of the reaction at the same time changes its sign.

These results of course agree with what is obtained analytically.

The following notation is used in all the figures: $AD = R$, $AH = \frac{R}{2}$, $EA = T$, $DL = mg$, $EL = mj_a$, $HL = mj_c$.

University of Michigan, Oct. 28th, 1911.



